Inverse Designed Plasmonic Metasurface with \textit{ppb}

Optical Hydrogen Detection

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ABSTRACT

Plasmonic sensors rely on optical resonances in metal nanoparticles and are typically limited by their broad spectral features. This constraint is particularly taxing for optical H₂ sensors, in which hydrogen is absorbed inside optically-lossy Pd nanoparticles and for which state-of-the-art detection limits are only at the low parts-per-million (ppm) range. Here, we overcome this limitation by inversely designing a plasmonic metasurface based on a periodic array of Pd nanoparticles. Guided by a particle swarm optimization algorithm, we numerically identify and experimentally demonstrate a sensor with an optimal balance between a narrow spectral linewidth and a large field enhancement inside the nanoparticles, enabling a measured hydrogen detection limit of 250 parts-per-billion (ppb). Our work significantly improves current plasmonic hydrogen sensor capabilities and, in a broader context, highlights the power of inverse design of plasmonic metasurfaces for ultrasensitive (gas) detection.
Introduction

Resonant optical sensors typically rely on wavelength shifts ($\Delta \lambda$) of their spectral features, such as peaks in transmission\textsuperscript{1,2} and reflection,\textsuperscript{3,4} induced by analytes. To allow an accurate determination of the peak position and its quantitative dependence on the analyte concentration, one requires sensors with high quality factors (Q-factors),\textsuperscript{5,6} defined as the ratios of their resonance frequency by the corresponding linewidth. Since Q-factors are inversely related to the linewidth, which represents the losses of the resonant system, numerous strategies have been proposed to reduce these losses, and therefore sharpen the resonances and decrease the readout noise of optical sensors.\textsuperscript{5,7} These approaches include the use of low-loss materials\textsuperscript{8,9} and the tailoring of the resonator geometry as in nanoparticles-on-mirror,\textsuperscript{10} whispering-gallery-mode microcavities,\textsuperscript{11} and periodic metal nanoparticle arrays.\textsuperscript{12,13} In particular, periodic nanoparticle arrays achieve high Q-factors by two processes: first, they reduce the radiative losses of individual nanoparticles by destructive interference of the coherently scattered radiation by the nanoparticles in the array; second, they redistribute the electromagnetic field into the surroundings, thus outside the individual metallic nanoparticles where losses originate.\textsuperscript{9,12,14–16}

This last condition benefits sensors probing phenomena occurring outside the metal nanoparticles, such as changes in the refractive index of the surrounding medium.\textsuperscript{17} On the other hand, the removal of the field from the metallic nanoparticles is unfavorable for other classes of plasmonic sensors that probe changes inside the metal; the so-called direct plasmonic sensors.

Emerging examples of direct plasmonic sensors are plasmonic hydrogen sensors based on palladium (Pd) nanoparticles and their alloys.\textsuperscript{2,18,19} These devices feature spark-free and room-temperature operation, efficient remote readout with small footprints, subsecond response time with excellent resistance to cross-contaminating and deactivating gases, and long-term
Mechanistically, these sensors rely on the barrierless dissociation of H₂ molecules at the surface of Pd nanoparticles and the subsequent intercalation of H atoms into the metal lattice. The corresponding change in dielectric function between pure Pd and Pd hydride leads to shifts in the localized surface plasmon resonance (LSPR) spectra of Pd nanoparticles, which are linearly proportional to the hydrogen concentration inside the particles. Unfortunately, due to the lossy nature of palladium, the LSPR of Pd nanoparticles is broad, with full-widths at half maximum (FWHMs) typically >300 nm for nanostructures with plasmonic spectra at visible or near infrared frequencies. Consequently, these broad peaks introduce inaccuracies in the determination of the sensing readout peak position, \( \lambda_{peak} \), leading to higher signal noise, \( \sigma \), and thus higher limits of detection (LoD), defined as the lowest analyte concentration measurable with a signal larger than \( 3\sigma \). In fact, the detection limit still remains a significant challenge for plasmonic (and optical) sensors, with the state-of-the-art only at single-digit ppm; a comparably inferior performance than electrical sensors where ppb detection limit has been reported (Supplementary Table 1). While ppm hydrogen sensitivity is appropriate for some applications, an ultralow detection limit, coupled with the abovementioned advantages of plasmonic sensing, is crucial for various application requiring local and early detection, such as hydrogen embrittlement in engineering structural materials, and intragastric hydrogen production in bacterial infections.

Here, we overcome the sensitivity bottleneck of optical hydrogen sensors by designing and experimentally demonstrating a sensor capable of detecting hydrogen gas down to the ppb level. Our sensing platform is based upon 2D periodic arrays of palladium nanoparticles that support collective surface lattice resonances (SLRs). These resonances emerge via the hybridization of the LSPRs of the individual nanoparticles and the constructive in-plane diffraction orders of the
incoming light, known as Rayleigh anomalies (RAs). Since RAs emerge from interference effects outside the metal nanoparticles, they are characterized by narrow spectral features that are therefore inherited by the SLRs. We employ inverse nanophotonic design—an algorithmic technique to find optical structures with set functional targets, to find sensor array configurations with the highest figure-of-merit (FoM), defined as the ratio between the SLR wavelength shift, $\Delta \lambda_{\text{peak}}$, and its FWHM. Critically, we find that the maximum FoM emerging from our evolutionary algorithm is not achieved by the array with the narrowest resonance, but rather by the array with an optimal balance between a narrow SLR and sufficiently large field enhancements inside the nanoparticles. This generic approach, which can benefit any direct plasmonic sensing platform, guides us to identify and experimentally demonstrate a sensor nanoarchitecture with a discernible signal down to 250 ppb; the lowest detection limit reported for an optical hydrogen sensor.

**Results and Discussions**

Despite their sensing potential, plasmonic SLRs have so far only been extensively studied on prototypical plasmonic metals, such as Au and Ag, with sensing applications limited to refractive index changes outside or at the surface of the metal. The use of SLRs for direct plasmonic sensing of phenomena occurring inside the metals requires the utilization of active plasmonic metals such as Y, Mg and Pd. Hence, as a crucial step towards our optimized plasmonic sensor, we first demonstrate the existence of SLRs in periodically-arranged Pd nanoparticles and characterize their optical spectra and field distributions. To this end, we fabricated an extensive set of square arrays of 45 nm high Pd nanodisks with varying diameters ($d = 70–180$ nm, steps of 20/30 nm) and pitch distances ($a = 300–600$ nm, steps of 50 nm) on fused silica ($n_{\text{sub}} = 1.46$). To allow efficient radiative coupling between the nanodisks by the in-
plane diffraction orders, an index-matching medium is essential.\textsuperscript{36} We thus coated the arrays with a 200 nm thick poly(methylmethacrylate) (PMMA) film ($n_{\text{PMMA}} = 1.48$). Besides having a suitable refractive index, PMMA is also serendipitously beneficial for Pd hydrogen sensors because it accelerates sorption kinetics by lowering the H\textsubscript{2} absorption energy into the Pd lattice and rebuffs other interfering and deactivating gases, such as O\textsubscript{2}, CO, NO\textsubscript{2}, and volatile hydrocarbons.\textsuperscript{2,44}

**Figure 1** shows the experimental extinction spectra of 42 Pd nanodisk square arrays (scanning electron microscopy, SEM, images in Supplementary Figure 1) alongside finite-difference time-domain (FDTD) calculations (see Methods) that accurately reproduce all spectral features in the measured data. In particular, we observe extinction spectra with one, two, or three peaks, depending on the nanodisk diameter and array pitch. The Figure also includes the calculated extinction spectra of the corresponding single-particles, highlighting how arranging the nanodisks in a periodic array results in distinct optical properties compared to their isolated counterparts. Particularly, as the pitch of the array, $a$, increases, the “main” peaks (as referenced to the array with $a = 300$ nm) universally redshift and narrow (Supplementary Figures 2-3). For example, for the $d = 180$ nm sample, its FWHM reduces by one order of magnitude from $\sim 650$ to $\sim 65$ nm. Furthermore, we observe the appearance of additional redshifting peak(s) at lower wavelength(s) when $a$ reaches 350 and 500 nm. Last, scrutinizing closely these different peaks as a function of diameter reveals contrasting behaviors. While “main” peaks redshift as $d$ increases, the peaks at lower wavelengths are relatively immobile (Supplementary Figure 2). This observation hints that the “main” peaks are SLRs that are dominated by contributions from the LSPR, and that the peaks at lower wavelengths are dominated by RAs, since their position depends solely on the particle-to-particle distance and not on the nanodisk diameter.
Fig. 1. Optical extinction spectra of Pd nanoparticles in a periodic array. A collage of experimental (red) and simulated (blue) extinction spectra at normal-incidence from Pd nanodisk square arrays of fixed height, $h$, of 45 nm and PMMA layer thickness, $t_{\text{PMMA}}$, of 200 nm. The pitch of the array, $a$, increases from left to right from 300 nm to 600 nm. The nanodisk diameter increases from top to bottom from 70 nm to 180 nm. For comparison, the leftmost panels plot the extinction cross-sections (in m$^2$) of the corresponding isolated single particles ($a = \infty$). Arranging the nanodisks in arrays results in distinct optical spectra compared to their isolated single particle counterparts. The spectra comprise peaks originating from hybrid RA-LSPR modes – the SLR, see main text for details. Dashed lines are a guide to the eye to the position of corresponding extinction peaks as function of particle diameter.

To further characterize the nature of the extinction peaks, we mapped the field distribution and optical dispersion relation of the array with $a = 550$ nm and $d = 180$ nm, which pronouncedly
features three extinction peaks (Fig. 2a, see also a similar analysis for $a = 300$ and 400 nm in Supplementary Figure 4). Fig. 2b depicts the FDTD-calculated field distribution map of the array at three different $y$-polarized excitation wavelengths corresponding to each of the peak wavelengths ($\lambda_1$–$\lambda_3$). At the two shorter wavelengths ($\lambda_1$ and $\lambda_2$), complex field distributions are found, with maxima lying in-between the nanodisks. These features suggest a strong contribution from the RA to the resonance, consistent with the discussion above. The excitation at the longest wavelength ($\lambda_3$) gives rise to field maxima in the vicinity of the nanodisks, suggesting a strong contribution of the LSPR to the resonance. Given such field distribution, these relatively localized but narrow peaks will emerge as the sensing peaks for direct plasmonic sensing of hydrogen in our Pd nanodisk arrays.

**Figure 2. Field distribution and optical dispersion relation of Pd nanoparticles arranged in a periodic array.** (a) Extinction spectrum of an array sample with $d = 180$ nm, $h = 45$ nm, $a = 550$ nm, and $t_{\text{PMMA}} = 200$ nm. (b) 2D maps of the normalized total field amplitude $|E|^2$ of the array at the mid-height of the nanoparticles and at different excitation wavelengths, as marked in panel (a). Excitation at wavelengths $\lambda_1$ and $\lambda_2$ generate field maxima far away from the nanodisks – a prominent characteristic in a RA mode. In contrast, excitation at $\lambda_3$ features field maxima
surrounding the nanodisks. Dashed lines outline the base of the nanodisks themselves. (c) 

Experimental and simulated wavelength-resolved optical dispersion represented as the 
extinction spectra of the array for different angles of incidence. The dashed lines indicate the 
different RA orders of the array. The LSPR wavelength of the corresponding single-particle 
counterpart is also plotted which crosses two lower RA orders.

After confirming the physical origin of the multiple peaks of our array, we carried out an angle 
dispersion extinction measurement (see Methods) and plot it alongside data from FDTD 
simulations (Fig. 2c). From the data we can determine the different RA orders that give rise to 
the optical properties of the array (see calculation of Rayleigh anomalies in the Supplementary 
Information). The spectral shape is influenced by the higher (±1,±1) modes at shorter 
wavelengths and by the (±1,0) and (0,±1) modes at longer wavelengths. The latter lower order 
 modes overlap with the LSPR deduced from the single-particle extinction peak at certain 
illumination angles. The coupling of the LSPR to the diffraction orders results in the narrowing 
of the resonance, while, as we show later below, maintaining its direct plasmonic sensing 
properties when exposed to H₂ gas.

Having established the ability to efficiently engineer the FWHM via SLRs in Pd arrays, we move 
on to design our hydrogen sensor with the aid of FDTD calculation coupled to an inverse design 
optimization algorithm. As an optimization parameter for the performance of our sensor we use a 

FoM defined as (Fig. 3a)

\[
FoM = \frac{\lambda_{\text{peak Pd H}_2} - \lambda_{\text{peak Pd}}}{\text{FWHM}_{\text{Pd}}}.
\]  

(1)
Our optimization aims at developing sensors capable of detecting H\textsubscript{2} at sub-ppm concentrations. At these concentrations and at room temperature, the Pd-H system will be in the so-called $\alpha$-phase, characterized by hydrogen concentrations in the metal typically lower than $\sim 1$ at.\%. To best model the optical properties of the palladium hydride phase, we therefore use the composition PdH\textsubscript{0.12}, corresponding to the lowest PdH\textsubscript{x} composition for which an accurate dielectric function is available in the literature.\textsuperscript{23} From Eq. 1, it is apparent that the highest FoM is obtained by finding an array configuration where the contributions from the LSPR (maximizing $\Delta\lambda_{\text{peak}}$ upon hydrogenation) and RA (narrowing FWHM) in their hybridized modes are optimized.

![Diagram](image)

**Figure 3. Finding the sensor parameters with the highest FoM through particle swarm optimization.** (a) Schematic of the working principle and the associated figure of merit of our plasmonic sensor. (b) Sketches of the four parameters defining the architecture of the Pd nanodisk array and their range used for the particle swarm optimization (PSO) algorithm. In
To efficiently pinpoint the structural parameter combination with the highest FoM within such four-dimensional searching space, we adopt a particle swarm optimization (PSO) algorithm combined with our FDTD calculations (Fig. 3b). This computational technique comprises
populations that together assess the parameter space, and subsequently influence each other to
move within this space to maximize the set goal (fitness parameter) that, in our case, is to
maximize the FoM. We utilize 10 populations that start with a random set of parameter values
and assess their corresponding FoM. In the following generations, each population moves to
other parameter values that result in a higher FoM (Fig. 3c). Running this process for 15
generations (see Methods), we move from an average FoM of 0.03 to 0.09, with single-best
populations reaching 0.11. The corresponding best sensor architecture is \( d = 124 \) nm, \( h = 20 \) nm,
\( a = 376 \) nm and \( t_{\text{PMMA}} = 300 \) nm (Fig. 3d), with \( \Delta \lambda_{\text{peak}} \) and FWHM of 32 and 296 nm,
respectively (see other populations at Supplementary Table 2 and Supplementary Figure 6).
Looking at the best sensor extinction spectrum (Fig. 3d), it is interesting to note that only the
LSPR-dominated peak responds to hydrogen, whereas the other peaks have lower LSPR
contributions and are therefore less sensitive to changes in the refractive index of the nanodisks
(Supplementary Figure 7). This finding further corroborates our interpretation of the origin of the
SLR peaks above. Finally, to appreciate the role of SLR excitation in obtaining sensors with high
FoM, we also calculate the optical spectra of the best sensors single-particle counterpart (i.e.,
similar nanodisk parameters but not in array). As shown in Supplementary Figure 8, the isolated
nanodisk features comparable \( \Delta \lambda_{\text{peak}} \), but suffers from an expansive FWHM of 498 nm, which
drops its FoM to 0.07.
We also numerically assess the FoM for array parameters in close proximity to the ones of the
best sensor architecture. In particular, we vary the pitch of the array, \( a \), and the diameter of the
nanodisks, \( d \), within \( \pm 6 \) nm, as these are the parameters that are prone to largest uncertainties in
real sample fabrication via electron-beam nanolithography (see Methods). As shown in Fig. 3e,
the FoM variation within the studied range is relatively small (0.09–0.13, \(~10\%\) from 0.11),
which guarantees us to obtain the expected sensitivity when translating the best sensor
parameters into a real sample. Furthermore, it is clear that there are actually $a$ and $d$
combinations that result in slightly higher FoM, which could be identified if the PSO generation
iteration would be expanded beyond 15 generations. However, there exists a complex
relationship between small structural changes in our arrays and peak positions and line-widths in
the corresponding extinction spectra. Given the relatively simple definition of our optimization
parameter, FoM, extending our algorithm routine to more than ~15 generations typically led to
coalescence of peaks and thus spuriously high FoMs originating from inaccurate assignment of
peak positions (Supplementary Figure 10). While beyond the scope of the present work, these
issues can be mitigated by a more rigorous definition of the FoM, peak, and the line-width in the
resulting optical spectra, by more stringent boundaries on the structural parameters of the
nanodisks, and by using a dielectric function of much smaller hydride concentration relevant to
the targeted $H_2$ concentration range of the sensor application.

As the final step of our work and guided by the PSO results, we experimentally realized the
optimized sensor design using electron beam lithography (Fig. 4a-b, Supplementary Figure 11,
and Methods) and assessed its detection limit to hydrogen. To this end, we exposed the sensor to
pulses of gradually decreasing $H_2$ concentration in Ar carrier gas (1000 ppm to 250 ppb, the
lowest attainable concentration in our setup) at room temperature and plot its associated $\Delta \lambda_{\text{peak}}$,
which is obtained through a Lorentzian fit$^2$ (Supplementary Figure 12 and Methods). As depicted
in Fig. 4a, the sensor responds positively to different $H_2$ concentrations, with a signal noise,$\sigma_{\text{sensor}}$, of 0.01 nm (Supplementary Figure 12). Due to this small noise, the sensor is able to
measure even the lowest 250 ppb pulse, making it the first optical hydrogen sensor to achieve
sub-ppm detection (Supplementary Table 1). Recalling LoD as the lowest hydrogen pressure
measurable with a signal larger than $3\sigma$, we extrapolate it to be $\sim 200$ ppb (Fig. 4b). We expect such sensitivity to also hold in air, thanks to the excellent O$_2$ sieving provided by PMMA.$^{2,48}$

**Figure 4. Ultralow detection limit with Pd periodic array sensor.** (a) $\Delta\lambda_{\text{peak}}$ response to stepwise decreasing H$_2$ concentration (1000 to 0.25 ppm) in Ar carrier gas at room temperature. Inset: zoomed-in version of the sensor response to 250 ppb H$_2$. (b) Measured $\Delta\lambda_{\text{peak}}$ as a function of H$_2$ concentration derived from (a). Gray dashed line is a guide to the eye and extrapolates the sensor response to the $3\sigma$ value (0.03 nm, red dashed line), indicating a LoD $\sim 200$ ppb (red dashed arrow). Inset: SEM image of the fabricated sensor. (c) and (d) are the data from a control quasi-random array sensor analogous to (a) and (b). The control sensor responds
comparably to the periodic array sensor but suffers from its higher noise. Hence, its LoD is $\sim 8$ times higher at 1.5 ppm.

As an important control, we fabricated an array with similar geometry parameters ($d = 124$ nm, $h = 20$ nm, and $t_{\text{PMMA}} = 300$ nm), but with the nanodisks dispersed quasi-randomly over the substrate rather than in a periodic lattice (Fig. 4c-d and Supplementary Figure 13). We compared the optical response of this control sensor exposed to H$_2$ pulses under similar experimental conditions as the periodic array. Consistent with the FDTD simulations (Supplementary Figure 8), the control sensor exhibits comparable $\Delta \lambda_{\text{peak}}$ with respect to the H$_2$ concentration (Fig. 4c). However, due to its larger FWHM, its $\lambda_{\text{peak}}$ determination results in a significantly higher noise, $\sigma_{\text{control}}$, of 0.08 nm (Supplementary Figure 14), which ultimately leads to a LoD of 1.5 ppm, nearly an order of magnitude higher than the detection limit of its array sensor counterpart (Fig. 4d). This comparison accentuates the critical impact of the narrow FWHM, here engineered through the use of optimized SLRs, for resolving $\Delta \lambda_{\text{peak}}$ signals at low concentrations.

Conclusions

In summary, we have used an inverse nanophotonic design approach to identify and experimentally demonstrate an ultrasensitive plasmonic hydrogen detector based on collective resonances in periodic arrays of palladium nanoparticles. The optimized sensor displays a non-trivial balance between a large optical response upon hydrogenation and narrow spectral features. The measured ppb limit of detection is an order of magnitude lower than any previous optical hydrogen sensor and becomes competitive with the more mature electrical sensors (Supplementary Table 1). The genericity of our strategy allows it to be combined with other
optimization approaches, including the use of more sensitive transduction materials such as PdAu,\textsuperscript{2,19,49,50} (eightfold more sensitive than Pd at low H\textsubscript{2} concentrations) or PdTa\textsuperscript{51} alloys, and advanced data fittings capable of producing lower signal noise.\textsuperscript{52} Furthermore, we have so far only explored a simple and generic figure-of-merit parameter during our optimization, namely the peaks shift divided by the linewidth. Our inverse design approach, however, also permits the optimization of nanoparticle arrays for sensing platforms using different readouts such as single-wavelength mode devices,\textsuperscript{53,54} opening the door to low-cost, ultrasensitive platforms. Beyond hydrogen sensing, our approach can be extended to arrays of surface-functionalized nanoparticles with resonances that are sensitive to the adsorption of specific gasses \textit{via} refractive index effects or chemical interface damping,\textsuperscript{55} with the potential to address a wider range of societal needs, from home safety to urban air pollution monitoring.\textsuperscript{56}
Acknowledgments

We acknowledge financial support from The Netherlands Organisation for Scientific Research through the NWO Vidi Award 680-47-550 and Vici Award 680-47-628, the Swedish Foundation for Strategic Research Framework project RMA15-0052, the Knut and Alice Wallenberg Foundation project 2016.0210 and the Swedish Energy Agency Project 49103-1. F.A.A.N. acknowledges support from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant Agreement No. 101028262. Part of this work was carried out at the Chalmers Micro- and Nanofabrication Laboratory MC2 and the Materials Analysis Laboratory (CMAL) under the umbrella of the Chalmers Excellence Initiative Nanoscience and Nanotechnology. We also thank Dr. Sven Askes and Ruben Hamans for critical reading of the manuscript.

Author contributions

F.A.A.N., P.B. and I.D. contributed equally. F.A.A.N. and A.B. conceived the project. F.A.A.N. and P.B. executed the FDTD calculation. P.B. developed and performed the PSO algorithm. I.D. and J.F. fabricated the sensors. F.A.A.N. and I.D. designed the sensing measurements. I.D. performed the sensing measurements. F.A.A.N. and G.W.C. measured the transmission and angle dispersion of the arrays. C.L. supervised I.D. and J.F. J.G.S. supervised P.B. and G.W.C. A.B. supervised F.A.A.N. and the project as a whole. F.A.A.N. performed data analysis and wrote the first draft of the manuscript. All authors commented on and edited the manuscript.

Additional information

Supplementary Information is available in the online version of the paper.

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Competing financial interests

C.L. is co-founder of a company that markets nanoplasmonic sensor-based technologies. The rest of the authors declare no competing financial interests.
Methods

Sensor fabrication and characterization. The samples of Pd periodic array were fabricated from a 4-inch fused silica wafer with electron-beam lithography, thermal evaporation, electron-beam evaporation, wet-chemical etching, reactive-ion etching, lift-off, and dicing. The steps involved included: (i) Using a 4-inch fused silica substrate (Siegert Wafer), a lift-off layer of 80 nm MCC NANO Copolymer EL4 (Microlithography Chemicals Corp.) was first spin coated and baked on a contact hotplate for 5 min at 180 °C. Following that, an imaging layer of 70 nm MCC NANO 950k PMMA A2 (Microlithography Chemicals Corp.) was spin coated and baked on a contact hotplate for 5 min at 180 °C. (ii) A 20 nm thick Cr layer was deposited with thermal evaporation (Lesker Nano 36) to enable electrical discharge during electron-beam exposure. (iii) The nanodisks were defined in the double resist layer on areas of 10×10 mm² with electron-beam lithography (Raith EBPG 5200) by exposing circles of 35 nm radius. Each circle was filled with 19 shots at a beam current of 50 nA and at a base frequency of 5.19 MHz. (iv) The 20 nm Cr discharge layer was removed by immersing the substrate for 60 s in Nickel/Chromium etchant (SunChem), followed by water rinsing and blow drying. (v) The exposed resist was developed for 60 s in MIBK 1:3 IPA solution, dried in N₂-stream, and descummed in oxygen plasma for 5 s at 50 W RF-power, 250 mTorr chamber pressure, and 40 sccm gas flow in a BatchTop Reactive Ion Etcher (PlasmTherm). (vi) To form the nanostructures, Pd were deposited through the resist mask with electron-beam evaporation at a deposition rate of 1 Å/s in a PVD 225 system (Lesker), lifted off in acetone for 24 h, rinsed in IPA and blow dried in N₂-stream. (vii) Finally, the wafer was diced (DAD3350, Disco) into individual chips of 10×10 mm². For the control quasi-random array sample, the fabrication procedures (steps, materials, and tools used) followed exactly the protocol reported in ref. 2. The only difference was the polystyrene beads used, that is, 120 nm sulfate latex, Interfacial Dynamics Corporation, 0.2 wt.% in Milli-Q water (Millipore). The SEM images were collected from glass samples coated with 5 nm Cr layer (Zeiss Supra 60 VP with secondary electron detector, working distance 4 mm, and an electron beam acceleration voltage of 7–15 kV).

Finite-Difference Time-Domain simulations. We used commercial Lumerical FDTD software to calculate the optical properties of both single and array of Pd nanodisks. We modeled the nanodisks as cylinders with a taper angle (the angle between the base and the side wall) of 65° to be close with the fabricated samples.57 The permittivity values of Pd and Pd hydride (PdH₁₂) were taken from the literature.55 The nanodisks were placed directly on top of a fused silica substrate (n = 1.46). On top of the substrate and embedding the particles, a PMMA layer was added, whose permittivity was obtained from an ellipsometry measurement.58 Finally, on top of this layer, there was air (n = 1). The simulations of the scattering efficiencies were done using a total-field scattered-field (TFSF) source with a broadband (400–1100 nm) beam incident from air and along the normal direction. The TFSF source divides the simulation region into two concentric volumes: one centered around the particle with the total fields, and another external where only the scattered fields propagate. Power transmission monitors were positioned around the TFSF source to calculate the scattering cross sections. The efficiency was calculated by dividing the former quantities by the geometrical cross section, i.e., the area of the cylinder perpendicular to the propagation vector k of the incident field. Perfectly matched layer (PML) boundaries were implemented in every direction. The simulations of the periodic arrays were performed using periodic boundary conditions in the x- and y-directions, and PML boundaries in the z-direction. The illumination consisted of a broadband (400–1100 nm) beam, approximated by a plane wave, which was incident normal to the array plane (the xy-plane) from air. To extract
the transmission, an $xy$ monitor was placed at the substrate side. Another $xy$ monitor was placed at the center of the particles to extract the fields. The polarization of the incident electric field was set along the $y$-axis. To extract the extinction ($i.e.$ 1 - transmission) dispersion data, several simulations with different incident angles were performed.

**Optical dispersion measurements.** An unpolarized broadband light source was used to illuminate the samples and investigate their optical dispersion. The light was focused onto the sample and collected with a Nikon L Plan 20x/0.45NA and a Nikon S Plan Fluor 40x/0.6NA objectives, respectively. Using a dedicated lens system, the back focal plane of the objective was imaged with an imaging spectrometer connected to a multiplying CCD camera (ProEM: 512B). The back focal plane contained the Fourier transform of the optical field transmitted by the sample upon illumination, $i.e.$ the angular dispersion of the transmitted light. The image on the CCD contained 2D angular information for all the wavelengths illuminating the sample. Closing the slit that controlled the light entering the imaging spectrometer allowed selection of one angular component and its spectral decomposition into the CCD. To get accurate wavelength resolution, a grating of 150 g/mm was used. This allowed $\pm 150$ nm range to be imaged for a selected wavelength center. To image the full spectrum of the sample ($400$–$1000$ nm) we measured spectra at several wavelength centers ($i.e.$ $470$, $620$, $770$, and $900$ nm, respectively). Using a polarizer before the illumination objective allowed us to select between TM and TE polarizations.

**Particle Swarm Optimization calculation.** To design the most sensitive hydrogen sensors, the FDTD method associated with the particle swarm optimization (PSO) algorithm was adopted. PSO is a robust population-based stochastic evolutionary computation technique, which is inspired by the natural social behavior and dynamic movements with communications of animal species (called particles) and looking for their requirements in a search space. Here PSO was employed to optimize the structural parameters of the plasmonic hydrogen sensor to yield the highest FoM defined by Eq. 1. To this end, we chose to use $\text{PdH}_0.12$ for the calculation of the hydride phase for the following reasons: (i) This is the lowest Pd hydride concentration whose dielectric function is available in the literature. (ii) At this concentration, the Pd hydride is still at the diluted $\alpha$-phase, with negligible lattice expansion. This condition prevents inaccurate calculation during FDTD simulation where the expansion of the nanodisk has to be included. (iii) The chosen hydride concentration is also in line with the targeted range of the hydrogen concentration. (iv) Lastly, the accompanied spectral change of the sensor at this hydride concentration was expected to be small enough so that it would be the same SLR peak that was considered, thus avoiding false $\Delta \lambda_{\text{peak}}$ determination when calculating the FoM, as we detailed later below.

To begin the optimization, the algorithm was initialized with 10 Pd/PdH$_{0.12}$ nanodisk arrays of random locations of parameters in their own spaces, which then were sent to the Lumerical FDTD platform, where the transmission was numerically evaluated. After that, FDTD sent the computed optical values back to the algorithm where the FoM was calculated, and produced the parameters for the next generation. The full technical description of the PSO used here is provided in the Supplementary Information.

Ideally, PSO should keep iterating until all particles converge to the global optimal solution instead of stopping at the 15th generation as in our present case here. However, we found that a number of populations updated their FoM through very large peak shifts and very broad FWHM...
that included two SLR different peaks. In the Supplementary Figure 10, we show an example for a population at the 18th generation. In this case there are two close SLR peaks in both Pd and PdH0.12 arrays at around 530 nm and 650 nm, respectively. In this case, the algorithm wrongly considered the lower wavelength peak for the case of Pd, and the longer wavelength peak for the case of PdH0.12, causing a wrong evaluation of Δλpeak. Furthermore, the FWHM was also calculated for two close SLRs. Consequently, in such case, we cannot correctly calculate the FoM since the parameters originated from two different peaks. Because this similar array began to appear in the 16th generation, we stopped the PSO after the 15th generations and confirmed that all the FOM calculated were from single SLR peak (Supplementary Figure 6).

**Hydrogen sensing measurements.** The sensors’ LoD determination was performed in a custom-made reactor chamber (effective volume ca. 1.5 mL) equipped with two fused silica viewports (1.33” CF Flange, Accu-Glass) that enabled transmission-mode optical monitoring. The detail of the chamber is reported in ref. 60. The transmission measurements were carried out through fiber-coupled, unpolarized halogen light source (AvaLight-HAL-S-Mini) and a high-resolution visible range spectrophotometer (Avantes Sensline Avaspec-HS-TEC). The H2 gas concentration was controlled by adjusting the flow rate (ν [mL/min]) ratio of 1000 ppm H2 (diluted in Ar) and 100% Ar using mass flow controllers (MFCs, Bronkhorst El-Flow Select series), see Supplementary Table S3. All experiments were carried out at constant 30°C, regulated via a PID controller (Eurotherm 3216) in a feedback loop manner, where the sample surface temperature inside the chamber was continuously used as input. As readout, the LSPR peak descriptors (λpeak) were obtained following the method we established earlier.2 In detail, a Lorentzian fit was applied to the wavelength range at ±60 nm around the LSPR peak in the measured optical extinction spectra. Despite the asymmetry of the global LSPR peak, a good fit (R2 > 0.97) was obtained, and thus the fit is appropriate to determine the λpeak (Supplementary Figures 12 and 14).

**Data availability**

All experimental data within the article and its Supplementary Information are available from the corresponding authors upon reasonable request.
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