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DOI
10.1021/acsami.8b22455

Publication date
2019

Document Version
Final published version

Published in
ACS Applied Materials and Interfaces

Citation (APA)

Important note
To cite this publication, please use the final published version (if applicable).
Please check the document version above.

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Direct Comparison of PdAu Alloy Thin Films and Nanoparticles upon Hydrogen Exposure

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ABSTRACT: Nanostructured metal hydrides are able to efficiently detect hydrogen in optical sensors. In the literature, two nanostructured systems based on metal hydrides have been proposed for this purpose each with its own detection principle: continuous sub-100 nm thin films read out via optical reflectance/transmittance changes and nanoparticle arrays for which the detection relies on localized surface plasmon resonance. Despite their apparent similarities, their optical and structural response to hydrogen has never been directly compared. In response, for the case of Pd$_{1-y}$Au$_y$ (y = 0.15–0.30) alloys, we directly compare these two systems and establish that they are distinctly different. We show that the dissimilar optical response is not caused by the different optical readout principles but results from a fundamentally different structural response to hydrogen due to the different nanostructurings. The measurements empirically suggest that these differences cannot be fully accounted by surface effects but that the nature of the film—substrate interaction plays an important role and affects both the hydrogen solubility and the metal-to-metal hydride transition. In a broader perspective, our results establish that the specifics of nanoconfinement dictate the structural properties of metal hydrides, which in turn control the properties of nanostructured devices including the sensing characteristics of optical hydrogen sensors and hydride-based active plasmonic systems.

KEYWORDS: nanostructuring, optical hydrogen sensing, metal hydride, plasmonics, thin films, nanoparticles, PdAu, X-ray diffraction

INTRODUCTION

The detection of hydrogen in a fast, reliable, and accurate manner is key for its safe handling in industrial processes and for its acceptance and implementation as an energy vector. In this context, optical hydrogen sensors have an inherent safety benefit because they do not require electrical contacts which may introduce sparks near the sensing area. In addition, they can be made small, relatively cheap and offer the possibility to spatially separate the readout from the sensing area.

To this end, two different nanoarchitectures have been proposed to optically track hydrogen: continuous thin films and arrays of nanosized particles. Both of these systems take advantage of a metal hydride-based sensing material, which hydrogenates upon an increase in partial hydrogen pressure, resulting in the change of its optical properties. However, the underlying physics of the generated optical contrast and signal readout of the two systems differs substantially. Whereas the readout of thin film sensors typically relies on changes in the optical reflectance or transmittance, the readout of nanoparticles relies on the excitation of localized surface plasmon resonances (LSPR) and the tracking of the corresponding “peak” in the optical spectrum, which broadens and shifts to longer wavelengths upon hydrogen sorption.

In the field of hydrogen sensors, PdAu alloys have, in particular, been considered as an effective sensing material for both thin films and nanoparticles. The alloying of the reference metal hydride palladium with gold significantly reduces or even completely eliminates the undesirable hysteresis from the first order metal-to-metal hydride transition, while it maintains the ability to dissociate hydrogen at room temperatures. A naive comparison of different studies of PdAu indicates that the performance in terms of hysteresis, sensing range, and sensitivity of thin film and nanoparticle based sensors is, quite surprisingly, substantially
shaped nanoparticles, as illustrated in Figure 1, when exposed to hydrogen. As the key results, by means of neutron reflectometry (NR) and quartz-crystal microbalance (QCM) measurements, we find a linear relation between the optical signal and the amount of hydrogen absorbed for both systems, and our analysis shows that the hydrogen solubility in the metal phase is significantly enhanced for the thin films compared to nanoparticles and bulk Pd$_{1-x}$Au$_x$. Furthermore, in situ X-ray diffraction (XRD) reveals that the origin of hysteresis in nanoparticles with Au concentrations up to $y = 0.15$ is an incoherent first-order transition between the dilute $\alpha$-Pd$_{1-x}$Au$_x$H$_x$ and high hydrogen concentration $\beta$-Pd$_{1-x}$Au$_x$H$_x$ phases. In contrast, in the corresponding thin film system, no signature of an incoherent phase transition is seen, however, substantial hysteresis is observed which persists up to $y = 0.30$ and spans a much wider pressure range. Because the diffractograms do not show two-phase behavior, we attribute the hysteresis purely to the plastic deformation due to substantial surface-clamping effects for thin films. These results highlight that the specifics of nanoconfinement dictate the structural properties of metal hydrides, which in turn controls the properties of nanostructured hydride-based devices, such as...
is qualitatively very similar to that of white light optical transmission of the for thin film exposure, relative to the transmission of the as-prepared sample \(\ell_{\text{pre}}\), (b) \(x\) in Pd\(_{1-x}\)Au\(_x\)H\(_y\) for Pd\(_{1-x}\)Au\(_x\)H\(_y\) nanoparticles as a function of the wavelength shift of the LSPR with respect to the as-prepared state \(\Delta\lambda_{\text{LSPR}}\) after ref 19.

![Figure 3](image.jpg)

Figure 3. Relation between the optical readout and \(x\) in Pd\(_{1-x}\)Au\(_x\)H\(_y\) for Pd\(_{1-x}\)Au\(_x\)H\(_y\) (\(y = 0.15–0.30\)) thin films and nanoparticles. (a) \(x\) in Pd\(_{1-x}\)Au\(_x\)H\(_y\) for Pd\(_{1-x}\)Au\(_x\)H\(_y\) thin films as a function of the changes in optical transmission relative to the optical transmission of the as-prepared sample \(\ell_{\text{pre}}\). (b) \(x\) in Pd\(_{1-x}\)Au\(_x\)H\(_y\) for Pd\(_{1-x}\)Au\(_x\)H\(_y\) nanoparticles as a function of the wavelength shift of the LSPR with respect to the as-prepared state \(\Delta\lambda_{\text{LSPR}}\) after ref 19.

the sensing characteristics of optical hydrogen sensors and hydride-based active plasmonic sensors.

### Optical Measurements

Figure 2 summarizes the partial hydrogen pressure and composition dependence of the optical readout of thin films and nanoparticles of Pd\(_{1-x}\)Au\(_x\) (\(y = 0.15–0.30\)) at \(T = 28^\circ\text{C}\). For thin films, we display in Figure 2a,b the change in the white light optical transmission of the film, \(\ell_{\text{r}}\), upon hydrogen exposure, relative to the transmission of the as-prepared sample \(\ell_{\text{pre}}\). We have considered both thin films without [Figure 1a] and with a 3 nm adhesion layer [Figure 1b], and as discussed in the Methods and Materials section, they feature highly similar results from the second hydrogenation onward. For the nanoparticles (grown without adhesion layer, Figure 1c), we display in Figure 2c the wavelength shift of the LSPR peak, \(\Delta\lambda_{\text{LSPR}}\) with respect to the metallic state \((P_{\text{H}} < 5 \times 10^7 \text{ Pa})\).

The optical results are in good agreement with the literature\(^{13,17,19}\) and reproduce the key features, that is, for both thin films and nanoparticles, the optical contrast and hysteresis upon exposure to hydrogen decreases with increasing gold concentrations. In particular, all compositions of the thin films and nanoparticles show a pronounced and monotonous optical response to the partial hydrogen pressures over a wide range of \(1 \leq P_{\text{H}} \leq 1 \times 10^8 \text{ Pa}\). As the upper limit of the sensing ranges of both Pd\(_{1-x}\)Au\(_x\) thin films and nanoparticles are limited by the maximum pressure accessible in our experimental setups, we conjecture that it may extend to (much) higher hydrogen pressures.

Interestingly, however, the optical measurements also clearly show dissimilarities between the two systems with respect to the: (1) sensitivity and (2) appearance of hysteresis. With respect to (1), the optical response to hydrogen is more gradual in thin films. On the other hand, the Pd\(_{1-x}\)Au\(_x\) nanoparticles show, especially at low Au concentrations, a more steplike response of \(\Delta\lambda_{\text{LSPR}}\) as a function of the hydrogen pressure, whereas the response of the two systems becomes more similar at higher Au concentrations.

With respect to (2), we observe hysteresis in the optical response of the Pd\(_{1-x}\)Au\(_x\) thin films across a wide pressure range which diminishes with increasing Au concentration and with increasing temperature [Figure S1]. However, it persists even for Pd\(_{0.70}\)Au\(_{0.30}\). In contrast, hysteresis in the optical readout of the nanoparticles is limited to Pd\(_{1-x}\)Au\(_x\) with \(y = 0.15, 0.20,\) and 0.25 while it is completely absent at \(y = 0.30\).

Furthermore, it occurs only in a narrow pressure region centered around \(P_{\text{H}} = 2 \times 10^3 \text{ Pa}\), that is, around the plateau pressure of bulk palladium.\(^{22}\) Consistent with previous research,\(^{23}\) we note that the disappearance of hysteresis for alloys with higher Au content occurs at lower temperatures, indicating a lower critical temperature [Figure S2].

The next step in the analysis is to establish whether the differences between the optical response of Pd\(_{1-x}\)Au\(_x\) (\(y = 0.15–0.30\)) thin films and nanoparticles to hydrogen originate from the different detection mechanisms that create the optical contrast, that is, light attenuation versus excitation of LSPR. We do so by measuring the optical transmission of the Pd\(_{1-x}\)Au\(_x\) nanoparticles using the same setups and procedures as the ones used for the thin film measurements. Figure 2d shows that the partial hydrogen pressure dependence of \(\ln(\ell/\ell_{\text{pre}})\) is qualitatively very similar to that of \(\Delta\lambda_{\text{LSPR}}\). Hence, clearly the differences between the Pd\(_{1-x}\)Au\(_x\) thin films and nanoparticles are not the result of the optical detection method but likely relate to different structural and thermodynamic properties, as we discuss below. In addition, these results illustrate that one may track the optical transmission of nanoparticles as alternative readout to \(\Delta\lambda_{\text{LSPR}}\) while maintaining its desirable properties in terms of limited-to-no hysteresis and fast response times.\(^{17}\)

### Structural Measurements

#### Hydrogen Solubility.

To evaluate whether the difference in response is related to dissimilar hydrogen solubility in the two systems, we examine the pressure dependence of the hydrogen content in Pd\(_{1-x}\)Au\(_x\) thin films by NR (thin films) and compare it to the one in nanoparticles recently established using a QCM.\(^{19}\) By comparing these data [Figures S3 and S4] with the optical measurements, we establish an important relation: in all cases, the optical response, either the change in the white light transmission or the wavelength shift of the LSPR peak, scales linearly and universally with the absolute amount of hydrogen content irrespective of the Au fractions in the alloy [Figure 3]. Such a linear scaling has been reported before for other pure metal hydrides\(^{9,19,24,25}\) but its appearance and especially the universality is not at all trivial. One might expect that this universal scaling holds in the case of a coexistence of two phases with varying fractions, but it is not directly clear why it holds in the present situation of an increasing hydrogen content in a solid solution of palladium—gold and hydrogen. In addition, a comparison of the magnitude...
of the changes in optical transmission of the thin films upon hydrogenation [Figure 2d] with the one of nanoparticles [Figure 2a] yields that, for a given hydrogen content, the change in optical transmission with respect to the unloaded state is for all compositions about 10 times larger for the thin films. This difference can be fully accounted for by the different coverage fraction of the substrate (≈15% instead of 100%) and thickness of the layer (25 nm instead of 40 nm) of the nanoparticles with respect to that of the thin film, confirming that the absolute amount of hydrogen absorbed by the metallic host dictates the change in optical transmission. The results empirically suggest that the effect of hydrogen on the optical properties is independent of (i) its concentration and (ii) the composition of the metallic host, that is, the gold concentration. The universal scaling between the optical response and hydrogen content has the convenient implication that one can infer the hydrogen content from the optical response for thin films/nanoparticles with the same thickness. Therefore, this allows us also to present the hydrogen content of the alloy on the right y-axes of Figure 2.

A second interesting aspect, the direct comparison of the hydrogen solubilities in Pd_{1−y}Au thin films and nanoparticles with the data for bulk Pd_{1−y}Au from ref 22, as displayed in Figure 4 for the case of Pd_{0.85}Au_{0.15} reveals that thin films exhibit a higher hydrogen solubility than both nanoparticles and bulk. This not only explains the observed larger optical contrast (and thus sensitivity in a sensor application) of the thin films but also allows us to draw an important conclusion: although size dependencies of the hydrogen solubility in metal hydrides have been reported before (see, e.g., refs 26−28), these results empirically suggest that the enhanced solubility of hydrogen at low hydrogen pressures for thin films is not solely the result of interface/surface effects because such effects should be comparable or even more pronounced for nanoparticles. Hence, as further elaborated below, we postulate that the enhanced solubility observed in thin films is related to the compression exerted by the clamping effect of the substrate, which is very sizable for thin films.

**In Situ XRD of the Metal-to-Metal Hydride Transition.**

To address the second aspect of the dissimilar properties exhibited by the Pd_{1−y}Au thin films and nanoparticles, the hysteresis, we employed in situ XRD. In Figure 5, the behavior of the ⟨111⟩ diffraction peak as a function of the hydrogen pressure is shown for Pd_{0.85}Au_{0.15} while Figure 6 summarizes the behavior of all-studied Pd_{1−y}Au compositions. Clearly, both the film and nanoparticles are textured in the ⟨111⟩ crystallographic direction but their behavior during the phase transition implies distinct structural differences.

In the thin films, increasing the hydrogen pressures leads to a continuous and gradual shift of the ⟨111⟩ diffraction peak to lower diffraction angles [Figure 5a]. This gradual increase of the lattice spacing $d_{111}$ suggests a coherent transition from the dilute Pd_{1−y}AuH_y phase to the same phase with a high hydrogen concentration. A similar behavior is observed for all other compositions [Figure 6a−c]. In contrast, the diffractograms of the nanoparticles plotted in Figure 5c show the superposition of two diffraction peaks for hydrogen pressures around $P_{H_2} = 1400$ Pa. This indicates phase coexistence of $\alpha$ and $\beta$-Pd_{1−y}AuH_y and thus the occurrence of an incoherent phase transformation for Au concentrations up to at least $y = 0.15$ for the nanoparticles [Figure 5c]. For Au concentrations $y \geq 0.20$, a single phase behavior is observed, as expected from bulk thermodynamics of Pd_{1−y}Au, where the first-order phase transition disappears above a critical Au fraction of $y \approx 0.18$.34

The observed first-order behavior of the phase transition should also be correlated to the hysteresis observed in the lattice constant—and, indeed, we observe a small hysteresis in the lattice constant of the nanoparticles with $y = 0.15$ [Figure 5d]. Remarkably, the hysteresis extends to $y = 0.20$ where still a very small hysteresis can be discerned [Figure 6d]. This behavior is in stark contrast to the thin films. While the second-order nature of the transition suggests no hysteresis at all, in fact, we observe it for all compositions [Figure 6a,b]. In addition, this $d_{111}$-spacing hysteresis extends over a much wider pressure range ($10^2 \leq P_{H_2} \leq 10^3$), that is, in a similar pressure range as where NR reveals a higher hydrogen solubility [Figure 4]. Apparently, in addition to the first-order phase transformation, there is an additional factor involved inducing hysteresis. It is particularly potent in the thin films and only weakly affects the nanoparticles.

We propose that the different natures of the phase transition in Pd_{1−y}Au alloy thin films and nanoparticles are related to substrate clamping. Accommodating hydrogen results in lattice expansion, which induces strains in the host metal lattice. In contrast to bulk materials, two-dimensional clamped films have to obey constraints on lateral expansion, leading to a very high in-plane stress and plastic deformation. As shown by Wagner and Pandt,36 strong compressive strain may lower the critical temperature of the $\alpha$-to-$\beta$ transition, which would explain the single-phase behavior of the PdAu-based thin films. Above the critical temperature, which decreases with increasing Au concentrations [Figure S2],35,38 there is no distinction between the $\alpha$ and $\beta$ phases and a solid solution behavior is expected over the whole hydrogenation range. On the other hand, because the nanoparticles are more free to expand laterally, the clamping effects and the related induced lattice strain should be much less pronounced as compared with thin films. Therefore, in the nanoparticles, the first-order $\alpha$-to-$\beta$ phase transition occurs under similar conditions as in bulk.

With respect to the observations related to hysteresis, normally its occurrence is related to first-order transitions in which one phase (e.g., the $\beta$ phase) nucleates in another phase (e.g., the $\alpha$ phase). Hysteresis then occurs due to the energy barriers involved in the nucleation process which prevent the transition to occur at thermodynamic equilibrium.39−41
However, here, we find that hysteresis is also present when the first-order behavior and related phase coexistence is completely suppressed. This may be a result of the volumetric expansion required to accommodate the hydrogen absorption. Because this volume change is translated into a thickness increase of the system for which substantial atomic rearrangements have to occur, these rearrangements involve mechanical work and plastic deformation of the film which, in turn, create a thermodynamic barrier that increases the splitting of the hydrogen absorption- and desorption branch of the hydrogenation cycle.\textsuperscript{35,36} In addition, the nucleation of domains, inducing locally large stresses, may also be hindered substantially by the clamping of the film to the substrate.\textsuperscript{42,43} Our data thus suggest that clamping induces hysteresis in thin films notwithstanding the continuous nature of the phase transition. In the nanoparticles, the clamping is much weaker and hence the hysteresis in the $d_{111}$-spacing extends to samples just slightly beyond the critical concentration of the first-order

![Figure 5](image-url) In situ XRD results of (a,b) Pd$_{0.85}$Au$_{0.15}$ thin films with a 4 nm Ti adhesion layer and (c,d) Pd$_{0.85}$Au$_{0.15}$ nanoparticles at $T = 28$ °C. (a,c) Diffactograms of thin film/nanoparticles measured for the hydrogen pressures indicated in the legend and for increasing pressure steps. (b,d) Partial hydrogen pressure dependence of the $d_{111}$-spacing of a Pd$_{0.85}$Au$_{0.15}$ thin film/nanoparticles as measured by stepwise increasing and decreasing the pressure. The continuous lines represent fits of a pseudo-Voigt function to the experimental data. As further detailed in this figure, the experimental data of the Pd$_{0.85}$Au$_{0.15}$ nanoparticles are fitted to a superposition of two pseudo-Voigt functions in the region where phase coexistence occurs.

![Figure 6](image-url) Hydrogen pressure $P_{H_2}$ dependence of the $d_{111}$-spacing at $T = 28$ °C as obtained from in situ XRD measurements on (a−c) thin films and (d−f) nanoparticles. (a,d) and (b,e) display the pressure dependence of the $d_{111}$-spacing of Pd$_{0.80}$Au$_{0.20}$ and Pd$_{0.70}$Au$_{0.30}$ respectively, as measured by stepwise increasing and decreasing the partial hydrogen pressure. (c,f) Partial hydrogen pressure dependence of the $d_{111}$-spacing of Pd$_{1-y}$Au$_y$ thin films/nanoparticles as measured by stepwise increasing the pressure.
phase transition. To this end, we also note that clamping may also play an important role in the kinetics of the (de)-hydrogenation process of metal hydrides and may account for the different response times observed between nanoparticles \(^8\) and thin films, \(^13\) together with the surface-to-volume ratio.

An important observation left unaddressed is the increase of the hydrogen solubility at low pressures in the thin films compared to the nanoparticles [Figure 4]. This effect, at first, is somewhat contradictory to our arguments above because the lattice compression in the thin films should make it more difficult for hydrogen to enter the lattice. In this respect, the expanded \(d_{111}\)-spacing [Figure 6] is a result of this uniaxial compression. Hence, we would expect a lower hydrogen concentration in the thin films as compared to the nanoparticles. The opposite is the case, which suggests that the uniaxial compression leads to an enhanced hydrogen absorption. While earlier experiments on comparable systems point in the same direction, \(^5\) further studies are needed to elucidate the details of the origin of this effect. Furthermore, short-ranged atomic order and the number and structure of defects in the material may also play a role. \(^44\) Our results hint that this might be the case, as different hydrogen solubilities are observed for the first and subsequent exposures to hydrogen [Figure S6].

Our results have important implications for the use of PdAu and other metal hydrides in applications such as optical hydrogen sensors. They illustrate that different ways of nanostructuring result in distinctively different sensing characteristics. Consequently, this dissimilar response provides engineers with an additional degree of freedom to tailor the properties of these sensing materials to specific needs. In addition, our results illustrate that one may track the optical transmission of nanoparticles as alternative readout to \(\Delta\sigma_{\text{ASR}}\) while maintaining its desirable properties in terms of limited-to-no hysteresis and fast response times [Figure 2d]. \(^17\)

In general, the best suited choice of metal hydride, the amount of nanostructuring, and the detection method depend on many factors such as the desired sensing range, operating temperature, response time, and pricing structure. The observation of a higher hydrogen solubility at lower hydrogen pressures \((P_{H_2} \lesssim 10^3 \text{ Pa})\) of thin films as compared to nanoparticles, and thus a more gradual optical response seems to be a distinct advantage of thin films. Indeed, the gradual and larger response at low pressures possibly results in a higher accuracy and a more pressure independent sensitivity of the hydrogen sensor. However, it comes at the price of increased hysteresis, reducing the accuracy with which one can determine the hydrogen pressure at room temperature. For this reason, Pd\(_{1-y}\)Au, nanoparticles may be a more favorable choice, particularly with \(y = 0.25\) and 0.30. These two compositions have the advantage that they are not prone to the highly undesirable first-order transition for \(y \lesssim 0.20\), and that they have a relatively large solubility and optical contrast at especially lower hydrogen pressures [Figure 2].

CONCLUSIONS

In conclusion, we have established the existence of substantial differences between the optical response of Pd\(_{1-y}\)Au, \((y = 0.15-0.30)\) thin films and nanoparticles to hydrogen, even when they have the exact same composition and are measured and analyzed in the same way. Hence, these differences do not result from the method of detection but arise from a different structural response to the hydrogen pressure. Compared with bulk and nanoparticles, thin films exhibit both a larger hydrogen solubility at low hydrogen pressures and a much more pronounced hysteresis, which spans a wider pressure range. These dissimilarities are likely related to the freedom of expansion of the involved system and the clamping of the film to the substrate. Whereas nanoparticles can expand relatively freely in all directions, thin films are confined due to their two-dimensional nature and the strong attachment to the support minimizes their ability to reduce stress imposed by hydrogen absorption through lattice strain. Thus, our results empirically suggest that the effect of the substrate clamping on the thin film response to hydrogen exposure is twofold: on the one hand the nature of the phase transition switches from an incoherent first-order transition to a coherent solid solution behavior; however, on the other hand, significant hysteresis between the hydrogen absorption and desorption branch is induced, very likely due to the additional thermodynamic barrier required to undergo the plastic deformations and atomic rearrangements required to accommodate the thickness change. In a wider perspective, our results illustrate that the thermodynamics of nanostructured materials may deviate considerably from continuous thin films and that this is not solely due to surface effects. This provides not only a caveat when utilizing these materials in real-world applications, as, for example, in optical hydrogen sensors or active plasmonic metamaterial devices but also provides an additional degree of freedom to tailor the properties of these materials to specific needs.

METHODS AND MATERIALS

Sample Preparation. Thin Films. The Pd\(_{1-y}\)Au, continuous thin films were fabricated by cosputtering without and with a Ti adhesion layer. The 40 nm thick PdAu and 3 nm thick Ti layers were deposited in 3 Pa of Ar by magnetron sputtering in an ultrahigh vacuum chamber (AJA Int.) with a base pressure of \(10^{-9}\) Pa. The samples for the optical and in situ XRD measurements were deposited on \(10 \times 10 \text{ mm}^2\) quartz substrates with a thickness of 1 mm, while the samples for NR were deposited on 3 mm thick 3” fused quartz substrates and with a surface roughness \(< 0.4\) nm. The substrates were rotated during the deposition to enhance the homogeneity. Typical deposition rates included 2.5 nm s\(^{-1}\) (69 W direct current (dc)) for Pd, 0.5–1.2 nm s\(^{-1}\) (10–24 W dc) for Au, and 0.05 nm s\(^{-1}\) (100 W dc) for Ti. The thickness of the layers was derived from the sputter rate that was calibrated by stylus profilometry (DEKTAK) on thick samples (>150 nm). The derived thickness is within 10% from the thickness obtained from the neutron and X-ray reflectometry (XRR) measurements (see below). Alternatively, thin film samples were prepared by sputtering layers of Pd and Au on top of each other. These samples were annealed for 2 days in a 96% Ar–4% H\(_2\) atmosphere that was brought from \(T = 25\) to 400 °C and subsequently back to 25 °C. Subsequent XRR and XRD measurements confirm a homogenous Pd\(_{1-y}\)Au layer and optical transmission measurements show a similar response to hydrogen over the entire pressure range as the cosputtered films.

In our analysis, we have considered both thin films with and without 3 nm titanium adhesion layer. In contrast to palladium thin films, \(^3\) the optical response of the second and subsequent exposures to hydrogen is not substantially affected by the inclusion of the Ti adhesion layer [Figure S7], suggesting that the inclusion of gold improves the adhesion to the substrate. In both cases, reproducible results are obtained from the second cycle onward, although the first exposures of the film with and without Ti layers differ considerably [Figure S6]. Differences between the first cycles are common to thin films, as they require, in general, a few cycles of exposure to hydrogen to show reproducible results owing to a settling of the microstructure.
The similar response for the second and subsequent exposure to hydrogen of the films with and without a Ti adhesion layer is further substantiated by the in situ XRD data, which display a similar evolution of the $d_{111}$-spacing during the third exposure to hydrogen [Figure S8]. Together with the optical data, these results show that, compared to palladium, the interaction with the substrate strengthens due to the addition of Au, which allows us to make thin film sensors with a high cycling stability ($\geq 140$ cycles, see Figure S9). Furthermore, the Ti layer appears to promote the preferential orientation of the PdAu film [Figure S10].

**Nanoparticles.** Disk-shaped Pd$_{1−\alpha}$Au$_\alpha$ nanoparticles with a diameter of $190$ nm and a thickness of $25$ nm were fabricated on glass substrates (Borofloat, Schott Scandinavia AB), following procedures detailed elsewhere. The absolute hydrogen pressure was monitored using two capacitive pressure sensors with an interval of $0.65$ nm. The LSPR hydrogen sensitivity experiments were carried out in an in-house-made vacuum chamber with UHV-compatible sapphire optical windows. The sensing experiments were carried out in an in-house-made vacuum chamber. Prior to the measurements, the chamber was outgassed multiple times (>10) with a hydrogen-vacuum cycle. The optical response of the thin films with and without a Ti adhesion layer is further substantiated by the in situ XRD data, which display a similar evolution of the $d_{111}$-spacing during the third exposure to hydrogen.

**Optical Measurements.** Optical Transmission. The optical transmission was measured using hydrogenography in combination with a three charge-coupled device (3 CCD) camera. The transmission was averaged over an area of $20 \times 20$ pixels, corresponding to $400$ mm$^2$. Five Philips 840 MR16 MASTER LEDs ($10/50$ W) with a color temperature of $4000$ K were used as a (white) light source. The partial hydrogen pressures of $10^{-5} < P_{H_2} < 10^3$ Pa were obtained by using $0.1, 4$, and $100$% $H_2$ in Ar gas mixtures. Typical gas flows included $20$ sccm for increasing pressure steps and $100$ sccm for decreasing pressure steps.

**Localized Surface Plasmon Reference.** The LSPR hydrogen sensing experiments were carried out in an in-house-made vacuum chamber with UHV-compatible sapphire optical windows. The absolute hydrogen pressure was monitored using two capacitive pressure sensors with an interval of $0.65$ nm. The LSPR hydrogen sensitivity experiments were carried out in an in-house-made vacuum chamber with UHV-compatible sapphire optical windows. The optical response of the thin films with and without a Ti adhesion layer is further substantiated by the in situ XRD data, which display a similar evolution of the $d_{111}$-spacing during the third exposure to hydrogen.

**Structural Measurements.** Neutron- and X-ray Reflectometry. Neutron reflectometry measurements were performed at the time-of-flight neutron reflectometers ROG, Reactor Institute Delft, Delft University of Technology, and Offspec, ISIS, Rutherford Appleton Laboratory. The measurements at ROG were performed with an incident angle of $8.5$ mrad, a Q-range of $0.10−0.65$ nm$^{-1}$, and a wave-vector resolution of $\Delta Q/Q = 0.04$. The measurements at Offspec were performed with an incident angle of $8.7$ mrad, a Q-range of $0.12−0.90$ nm$^{-1}$, and a wave-vector resolution of $\Delta Q/Q = 0.05$.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors wish to thank the ISIS support staff for their valuable technical assistance. C. de Vroege and B. Boshuizen are acknowledged for renewing the software of the hydrogenation cell for the NR and in situ XRD measurements. The NR experiments at the ISIS Pulsed Neutron and Muon Source were supported by a beamtime allocation from the Science and...
Technology Facilities Council (RB 1700068) and the corresponding data are available at doi.org/10.5286/ISIS.E.66388270. The contributions by F.A.A.N. and C.L. are financially supported by the Swedish Foundation for Strategic Research framework project RMA15-0052 and the Knut and Alice Wallenberg Foundation project 2016.0210.

REFERENCES