Optical fiber hydrogen sensor using metasurfaces composed of palladium

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Palladium-based hydrogen sensors have been typically studied due to the dielectric function that changes with the hydrogen concentration. However, the development of a reliable, integral, and widely applicable hydrogen sensor requires a simple readout mechanism and an optimization of the fast detection of hydrogen. In this work, optical fiber hydrogen sensing platforms are developed using an optimized metasurface, which consists of a layer of palladium nanoantennas array suspended above a gold mirror layer. Since the optical properties of these palladium nanoantennas differ from the traditional palladium films, a high reflectance difference can be achieved when the sensor based on the metasurface is exposed to the hydrogen atmosphere. Finally, the optimized reflectance difference ΔR of ~0.28 can be obtained when the sensor is exposed in the presence of hydrogen. It is demonstrated that this integrated system architecture with an optimized palladium-based metasurface and a simple optical fiber readout system provides a compact and light platform for hydrogen detection in various working environments.

Keywords: hydrogen detection; metasurface; palladium; optical fiber sensor.
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1. Introduction

Hydrogen (H2) has attracted lots of attention as a future energy source, especially due to its high energy-density, carbon-free, and pollution-free characteristics[1,2]. However, H2 is flammable and has low ignition energy. At room temperature and pressure, H2 exhibits a wide explosion range for concentrations (4%–75% by volume) coupled with a large flame propagation speed. Furthermore, as a colorless, odorless, extremely volatile gas, it diffuses very fast and easily, so it may eventually leak out of its container due to its small molecular size[3]. Thus, fast leaks detection equipment for all H2-related systems is required because of such safety reasons.

Electrical H2 gas sensors with an electrical readout employ the change in electrical conductivity upon H2 absorption in metal. However, such electrical sensors can only show enhanced sensitivity at high working temperatures, thus raising safety issues. Alternatively, in optical sensing schemes, the change in reflectance and/or transmittance of H2-absorbing materials is detected[4]. A fiber-based readout has arisen as well, providing numerous advantages such as safety, corrosion resistance, and suitability for remote sensing. To date, optical fiber H2 sensors have demonstrated high performance, which propelled the technique to the hazardous areas of certain industrial environments, such as H2 fuel filling stations or nuclear waste repository environments[5–7]. However, such optical fiber sensors have to use special architectures to interact with the outer medium. Typical optical fiber structures, including fiber gratings[8,9], tapered fibers[10], D-shape[11,12], and U-bent[13], limit large-scale production and promotion.

In contrast with other materials solving hydrogen sensitivity such as tungsten trioxide (WO3)[14] and zinc oxide (ZnO)[15], palladium (Pd) is a particularly suitable and widely used functional material for specific H2 detection because the reversible phase transition depends on the ambient H2 concentrations at room temperature[16]. Hydrogenation happens due to a change in the dielectric function with the change from Pd to PdHx. Since the H atoms occupy interstitial lattice sites (α-phase) and even saturate the Pd lattice (β-phase) at high H2 concentrations, an increase of the lattice constant of over 10% would be achieved[17].

In recent years, two main types of Pd-based H2 sensors are thin films and plasmonic nanoparticles[18–21]. In these two cases, the transmittance/reflectance and wavelength shift monitor can
be adapted to analyze the \( \text{H}_2 \) concentration, respectively. The relative simplicity of reflectance measurements makes such Pd-material-based \( \text{H}_2 \) sensing systems more suitable for large-scale, integral sensor applications. However, Pd thin films suffer strongly from undesirable effects such as a hysteresis in the loading and unloading of \( \text{H}_2 \) and deactivation through poisoning by other gases. On the other hand, sensors based on Pd nanoparticles, which are synthesized by chemical synthesis, are limited by poor reproducibility due to the uncontrollable surface morphology of nanoparticles in chemical synthesis. Using nanoantennas is an effective alternative because of the controllable surface morphology owing to the fabrications with nanometer level accuracy, such as lithography, nanoimprinting, and others. Additionally, different nanostructure geometries and advanced optimization methods based on mathematics can be investigated to enhance the \( \text{H}_2 \) sensitivity and to calculate the suitable parameters for the complex nature of the array manufacturing to ensure the reproducibility of the sensor. Recently, \( \text{H}_2 \) detection using nanoantennas and hydrogenation of thin films have been demonstrated as well\[^{17,22-26}\].

In the present work, we demonstrate an optical fiber \( \text{H}_2 \) gas sensor consisting of a commercial multi-mode optical fiber and a metasurface attached to the fiber tip. The optimized metasurface is composed of a layer of Pd nanoantennas suspended above a gold (Au) mirror layer. The reflectance of the Pd-based metasurface is \( \sim 0.6 \), and it shows a clear reflectance or a power change of \( \sim 0.28 \) or \( \sim 3.26 \text{ dB} \) after it is exposed to \( \text{H}_2 \), indicating an excellent hydrogenation response performance. Moreover, a fiber-based reflectance readout method can be adopted to analyze the \( \text{H}_2 \) concentration, respectively. The relative simplicity of reflectance measurements makes such Pd-material-based \( \text{H}_2 \) sensing systems more suitable for large-scale, integral sensor applications. However, Pd thin films suffer strongly from undesirable effects such as a hysteresis in the loading and unloading of \( \text{H}_2 \) and deactivation through poisoning by other gases. On the other hand, sensors based on Pd nanoparticles, which are synthesized by chemical synthesis, are limited by poor reproducibility due to the uncontrollable surface morphology of nanoparticles in chemical synthesis. Using nanoantennas is an effective alternative because of the controllable surface morphology owing to the fabrications with nanometer level accuracy, such as lithography, nanoimprinting, and others. Additionally, different nanostructure geometries and advanced optimization methods based on mathematics can be investigated to enhance the \( \text{H}_2 \) sensitivity and to calculate the suitable parameters for the complex nature of the array manufacturing to ensure the reproducibility of the sensor. Recently, \( \text{H}_2 \) detection using nanoantennas and hydrogenation of thin films have been demonstrated as well\[^{17,22-26}\].

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2. Methods

Figure 1(a) presents the schematic of the \( \text{H}_2 \) sensing metasurface architecture. In this design, promising geometry consists of an array of Pd nanostructures, which is separated by a dielectric spacer layer from the Au film. The Au film, here, acts as a mirror, and the magnesium fluoride (MgF\( \text{2} \)) is employed as a dielectric spacer layer. The dielectric spacer layer is used to generate a metal–insulator–metal (MIM) meta-atom, which can be treated as a Fabry–Pérot cavity to increase reflectivity\[^{27}\]. Figure 1(b) shows the scheme of the \( \text{H}_2 \) sensor, which consists of a metasurface and a fiber flange plate that serves as a connector to the optical fiber. Thus, a simple optical fiber-based readout mechanism can be used, which is based on the broadband light source with a working range of 1250–1600 nm and the power meter to monitor the reflection intensity. Moreover, a polarization controller (PC) was placed upstream of the circulation to adjust and orient the state of the polarization of light so as to provide linear polarization.

Using this nanostructure layout and optical fiber-based readout mechanism, the optical reflectance \( R \) can be read out and optimized through careful tuning of the design parameters. In fact, the highest \( \text{H}_2 \) sensitivity would be achieved by maximizing the absolute reflectance difference. In this work, we thus focus on optimizing the relevant design parameters, e.g., the diameter of Pd nanodisks, the thickness of a MgF\( \text{2} \) spacer, to achieve a maximum \( \Delta R \). Specifically, we perform numerical calculations on a model system\[^{28}\], where the Pd nanoantenna is on a MgF\( \text{2} \) spacer and an Au mirror, to obtain a better understanding of the optical response and the underlying physical principles and to predict an optimum sensor design.

3. Results and Discussions

Numerical calculations with the finite difference time domain (FDTD) method have been carried out to gain better insight into the reflectance of the Pd nanoantennas. To investigate the behavior of the reflectance difference \( \Delta R \) due to the hydrogenation of the Pd-based metasurface, we perform simulations in Lumerical FDTD on the same system as in Fig. 1(a) with the dielectric function of the Pd disks (\( \alpha \)-phase) and PdH disks (\( \beta \)-phase), where the refractive index of Pd and PdH is from the open access refractive index database\[^{29}\]. Additionally, the size of the PdH disk, which we considered here in the
Curves indicate that the reflectance increases with the red-shifted wavelength \( \lambda \), and a blue curve is displayed in Fig. 3, and a blue curve is the case of wavelength \( \lambda \) parameters of the reflectance of Pd hydride (black line), which considered the incident light. Additionally, the wavelength spectrum of the reflectance of Pd (red line) as a function of varying wavelengths of incident light is shorter. These results show that a higher reflectance difference \( \Delta R \) can be obtained at a short wavelength of the incident light. As Fig. 3 shows, the highest reflectance difference \( \Delta R \) corresponding to 0.168 can be achieved when the wavelength of the incident light is 586 nm. Compared with the results of nanoantennas, this maximum \( \Delta R \) is much lower. Furthermore, unfortunately, the reflective spectrum is fixed for Pd film, and commercial communication optical fibers have a high loss at such lower wavelength. On the other hand, the working wavelength for a Pd-based metasurface can be shifted artificially to match the working wavelength of optical fibers by changing the size parameters of the nanoantenna.

Figure 4(a) presents the wavelength spectra of reflectance as a function of varying thicknesses of the spacer layer \( l_{\text{spacer}} \). The diameter and thickness of the Pd disk are 250 nm and 20 nm, respectively. After considering the parameters of the \( \beta \)-phase, the counterpart’s pseudocolor plot of Pd hydride can be seen in Fig. 4(b). Furthermore, reflectance difference \( \Delta R \) as a function of wavelength \( \lambda \) and varying thicknesses of spacer \( l_{\text{spacer}} \) can be seen in Fig. 4(c).

The positions of two exemplary \( \Delta R \) maxima of \( \sim 0.25 \) are indicated in Fig. 4(c). Both of these positions are located at the wavelength of 1200 nm and 1320 nm with the same spacer thicknesses of 150 nm. Nevertheless, these positions are not the highest or lowest reflectance of the Pd or Pd hydride, as shown in Figs. 4(a) and 4(b). A key feature of the system can find that the highest reflectance differences can be obtained via tuning the thicknesses of the spacer layer. Even though, the thickness of the spacer layer should be chosen carefully, because it could decrease the interaction as well. In particular, a response maximum very close to a region of low response cannot be chosen, since a deposition technique with high accuracy is required. The envisioned readout wavelength of the sensor, the working range of the optical fiber, should be taken into account at the same time. In this case, the reflectance difference \( \Delta R \) of \( \sim 0.23 \) can be achieved when the spacer thickness is 150 nm and the wavelength is 1300 nm, which is located at the communication window of the common multi-mode optical fiber, as...
shown in Fig. 4(c). Instead of the single-mode optical fiber, here, a multi-mode fiber optical fiber should be used, because the mode field distribution, which covers the area of the metasurface, is required. A multi-mode optical fiber for the working wavelength of 1300 nm (OM1, Changfei Optical Fiber and Cable Co., Ltd.) would be used.

A further simulation was performed to investigate the influence of the mode field distribution of the optical fiber. The mode field distribution was firstly calculated when the wavelength of incident light is 1300 nm using the COMSOL Multiphysics for influence evaluation. As the results show, the diameter of the mode field distribution is 0.28 can be reached when exposed to the sensor in the presence of H2. Together with the intrinsic features of optical fibers[33], this Pd-based metasurface with an optical fiber readout system provides a promising platform for remote and harsh access H2 detection. Moreover, the mechanism of sensor performance is a possibility to tune its spectral range of operation by the diameter and thickness of the specificity recognition materials to make this design applicable to other molecular detection applications or to positively affect the interaction between biomaterials and cells.

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