

Pd₈₀Co₂₀ Nanohole Arrays Coated with Poly(methyl methacrylate) for High-Speed Hydrogen Sensing with a Part-per-Billion Detection Limit

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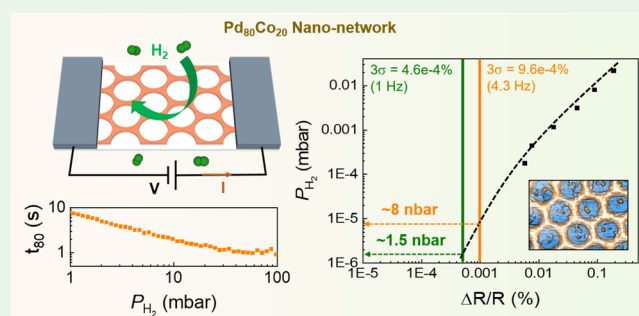
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ABSTRACT: As hydrogen gas increasingly becomes critical as a carbon-free energy carrier, the demand for robust hydrogen sensors for leak detection and concentration monitor will continue to rise. However, to date, there are no lightweight sensors capable of meeting the required performance metrics for the safe handling of hydrogen. Here, we report an electrical hydrogen gas sensor platform based on a resistance nanonetwork derived from Pd-Co composite hole arrays (CHAs) on a glass substrate, which meets or exceeds these metrics. In optimal nanofabrication conditions, a single poly(methyl methacrylate)(PMMA)-coated CHA nanosensor exhibits a response time (t_{80}) of 1.0 s at the lower flammability limit of H₂ (40 mbar), incredible sensor accuracy (<1% across 5 decades of H₂ pressure), and an extremely low limit of detection (LOD) of <10 ppb at room temperature. Remarkably, these nanosensors are extremely inert against CO and O₂ gas interference and display robust long-term stability in air, suffering no loss of performance over 2 months. Additionally, we demonstrate that the unique nanomorphology renders the sensors insensitive to operation voltage/current with diminutive power requirement (~2 nW) and applied magnetic field (up to 3 kOe), a crucial metric for leak detection and concentration control.

KEYWORDS: magnetic hydride resistance nanonetwork, electrical hydrogen sensor, high performance gas sensor, ppb limit of detection, composite hole arrays



INTRODUCTION

Hydrogen (H₂) gas plays a key role in modern society since it is required in many essential chemical processes.^{1,2} H₂ gas also has the potential to be a dominant energy carrier due to its high gravimetric energy density, sustainability, and lack of carbon emissions upon consumption.^{3,4} As H₂ generation and hydrogen fuel cell technologies continue to develop,⁵ the demand for H₂ sensors for safely handling H₂ gas in all stages of the hydrogen-based economy, including production, distribution, storage, and utilization, will also continue to rise.^{2,3} In this context, H₂ sensors with good stability, high sensitivity, rapid response time, and cost efficiency are highly desirable for leakage detection and concentration controls.² Various methods for H₂ detection have been proposed and intensively studied, including, but not limited to, electronic, mechanical, optical, acoustic, electrochemical, and thermal measurements.^{6,7} Among these methods, electric resistance-based sensors have been widely used in the gas sensing technology for decades due to the advantages of wide detection range, rapid response, very good selectivity, long-term stability, ease of use, and cost efficiency.⁸

Palladium (Pd) is the most common hydride-metal for electric sensor applications due to its rapid response, large H₂ adsorption, room temperature reversibility, and relative inertness.⁹ However, it has some critical drawbacks. Pure Pd-based sensors seriously suffer from hysteresis effects due to the development of large strain-inducing phase boundaries as hydrogen diffuses into and occupies interstitial sites within the metallic lattice.¹⁰ This hysteresis causes low-specific readout and hence reduces the sensor accuracy in the α - β mixed phase transition region, typically occurring at the H₂ pressure range of around 10 mbar,^{11,12} referred to as the “plateau region” due to the flattening of the optical and electronic response.^{13–15} Due to large volumetric expansion/contraction upon hydriding/dehydriding, repeated H₂ sorption cycles can cause

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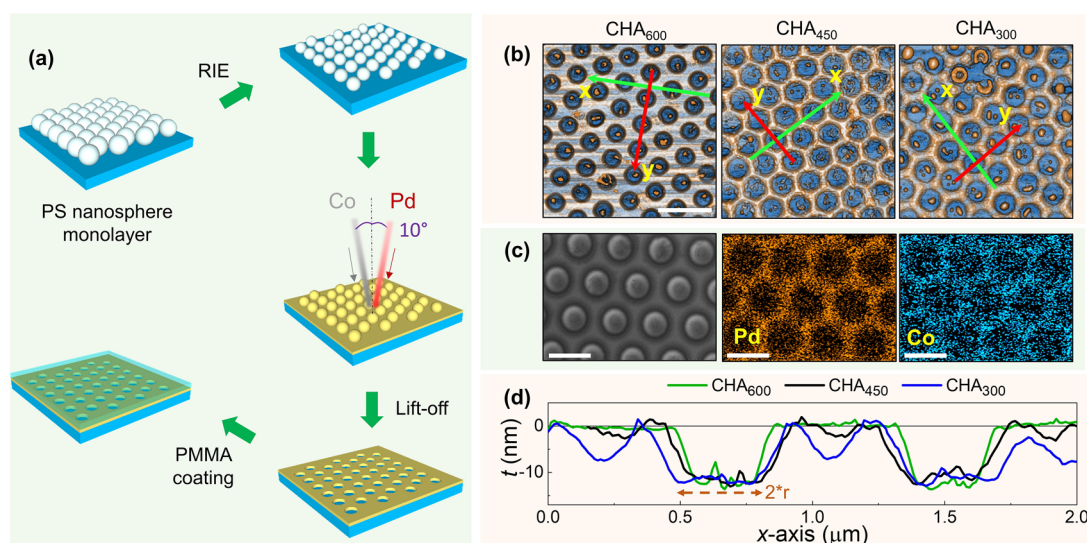


Figure 1. (a) Fabrication process of the CHAs and (b) representative atomic force microscopy (AFM) images of the CHAs with different reactive ion etching (RIE) times. (c) Top-view scanning electron microscope (SEM) images and energy-dispersive spectroscopy (EDS) elemental maps of $\text{Pd}_{80}\text{Co}_{20}$ CHA_{450} . The scale bars correspond to 500 nm. (d) Line profile measurement along the x -axis (green lines in panel (b)), where $t = 0$ is chosen at the top position of the CHA.

hydrogen embrittlement in Pd that affects the long-term stability of the sensor.^{16,17} Finally, hydrogen diffusion into the interstitial sites in pure Pd is typically slow, especially in its plateau region, due to the existence of a large strain-induced energy barrier upon H_2 sorption; therefore, the response time of the pure Pd-based sensors upon (de)hydrogenation is relatively slow. It is possible to minimize these drawbacks by the incorporation of alloying metals, such as Co, Ni, or Au,^{17–21} and/or the use of nanoscale structures.^{9,17} Owing to the difference in lattice constants of metals, serious nanoscale imperfections such as grain boundaries and dislocations are more likely to be formed in the alloy, leading to several key advantages.^{22,23} First, the imperfections may lower the H_2 sorption activation energy due to the reduction of the strain-induced energy barrier and may function as a fast diffusion path for the absorbed hydrogen atoms (large hydrogen permeability), enabling a faster response time for the alloy.^{17,22,24} Second, the imperfections might compensate for the lattice strain upon (de)hydrogenation, suppress the structure deformation, and therefore prolong the sensor stability upon sorption cycles.^{16,25,26} Finally, the plateau region in the pressure-sensitivity isotherm may be shifted to higher or lower pressures (e.g., Pd-Ni²⁷ or Pd-Au,^{15,19} respectively). Such shifts would remove the hysteresis behavior out of the detection range (1–100 mbar H_2 pressure), creating a reversible readout and an increase in the sensor accuracy.

Since the diffusion coefficient of hydrogen in Pd alloys is still limited, in order to further improve the sensing performance, especially enhance the response time, the use of nanoscale device structures has been extensively exploited to significantly increase the surface-to-volume ratios (SVRs) of the hydride materials, thus significantly shortening the hydrogen diffusion path to the interstitial sites. Such an increased SVR can also increase the hydrogen adsorption sites, reduce the enthalpy of formation/dissociation, suppress the dislocation nucleation at the free surface upon hydrogenation, and therefore further prevent the hydrogen embrittlement, and enhance the response and release time.^{24,25} Several nanostructures, including nanowires,^{28–35} nanotubes,³⁶ nanoparticles,³⁷ film

nanogaps,^{38,39} and nanonetworks,³⁵ have been proposed and implemented. Prior work has also demonstrated that the sensing kinetics of thin Pd-based sensors are strongly enhanced through encapsulating with a nanoscale polymer layer, yielding faster response rates.¹⁹ The faster kinetics are a result of the polymer–metal interface, which reduces the activation barrier for hydrogen absorption from surface to subsurface sites.¹⁹ Polymer coatings can also enhance the selectivity of Pd-based nanosensors to H_2 due to differential permeability and reject poisonous gases such as CO, CH_4 , and NO_2 .⁴⁰ However, the desired operational performance requirements for H_2 sensors have rarely been achieved in these studies.⁴¹

In this report, we design and fabricate Pd-Co composite hole array (CHA) nanoscale structures using shadow nanosphere lithography and characterize their performance as an electric hydrogen sensing platform.^{42,43} The CHA platform is a hexagonal resistance nanonetwork where the elementary resistance nanoscale size and shape can be tuned by the nanosphere size. The Pd-Co alloy rather than Pd-Au(Ag) is chosen because of the following reasons. First, the plateau region upon (de)hydrogenation of the Pd-Co-based sensor occurs at very high H_2 pressures (~ 1 bar),²⁷ allowing for high accuracy sensing readout spanning more than 5 orders of H_2 concentration/pressure. Second, our recent optical measurement shows that the response time upon hydrogenation in magnetic hydrides is an order of magnitude faster than that in the nonmagnetic alloys such as Pd-Au and Pd-Ag under the same conditions.⁴⁴ This superior performance is likely related to a greater metal–hydrogen bond strength in magnetic materials, which could facilitate dissociative chemisorption of H_2 .⁴⁵ Finally, the use of magnetic hydrides may give us an extra degree of freedom for manipulation of the sensing electrical signal by a magnetic field. At an optimal $\text{Pd}_{80}\text{Co}_{20}$ composition and CHA nanostructure, a single poly(methyl methacrylate)- (PMMA)-coated CHA nanosensor exhibits a response time (t_{80}) of 1.0 s at 40 mbar (lower flammable limit concentration), faster than 7.5 s over the entire detection range (1–100 mbar), and has a high sensor accuracy of less than 1% and an extremely low limit of detection (LOD) of <10

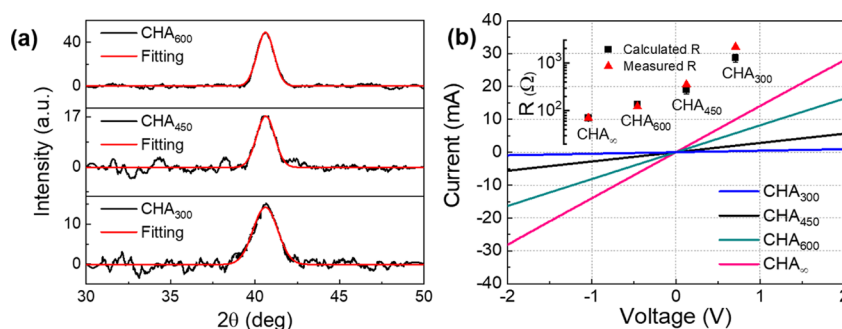


Figure 2. X-ray diffraction (XRD) spectra of alloy (111) peaks of CHA sensors. The red curves are fit by a Gaussian function. (b) I – V characteristics of the CHA sensors. The red solid triangles in the inset are the resistance of each sensor, while the black squares are the relative resistance calculated based on the device geometry.

ppb. Remarkably, the nanosensor possesses very good short-time stability and robust long-time stability when stored in nitrogen gas or air for 2 months. Finally, the sensor performance is insensitive to the operational voltage/current with tiny power consumption in the order of nW, and applied moderate magnetic field, and potentially has good selectivity against O_2 , humidity, and CO due to the poisonous gas filtration characteristics of the PMMA layer.¹⁹ The superior performance of the CHA nanosensor makes it one of the most promising electrical sensing platforms reported in the past decade (see Table S4).

RESULTS AND DISCUSSION

The nanofabrication process for the Pd-Co CHA is illustrated in Figure 1a, similar to those reported in the literature^{46–48} and described in detail in the Materials and Methods. Four types of $Pd_{80}Co_{20}$ -based nanosensors, CHA_t , with the same area of $5 \times 10 \text{ mm}^2$ and nominal thickness of 15 nm were fabricated, where t denotes the reactive ion etching (RIE) time in the unit of second, in which $t = \infty$ s corresponds to the $Pd_{80}Co_{20}$ thin film-based sensor. The RIE time dictates the diameter of the initial nanoscale polystyrene (PS) positive template and therefore the diameter of resultant nanoholes, where increasing the RIE time corresponds with a decreasing diameter (Table S1). The $Pd_{80}Co_{20}$ composition was first chosen as it exhibits large hydrogen permeability while maintaining sufficiently large sensitivity,⁴⁹ but the effect of different composition and smaller CHA thicknesses is considered here as well. The nanoscale geometries of the CHA_{300} , CHA_{450} , and CHA_{600} sensors were analyzed using atomic force microscopy (AFM). The hexagonal nanohole arrays with well-defined nanohole sizes are clearly shown in the AFM images, Figure 1b. The line profiles along the x -axis (green line) and its orthogonal y -axis (red line), shown in Figure 1b, are extracted and plotted in Figure 1d and Figure S1, respectively. The relatively sharp transitions between nanoholes and coating indicate that this nanoscale production method yields good coverage and uniform deposition. However, due to the setup in the deposition system, the fluxes of Pd and Co vapors impinge the substrate at an incident angle of $\sim 10^\circ$ from the opposite side (Figure 1a) during the electron beam evaporation and will cause an intrinsic shadowing effect for the etched PS nanospheres. As shown in Figure S2, the orientations of the shadows caused by Pd and Co vapors are different, and the film deposited onto the substrate via PS nanospheres can be divided into three regions: Pd-rich region, two-beam co-deposition region, and Co-rich region. To ensure the good

mixing of the Pd and Co, the substrate was rotated at 30 rpm azimuthally. Such a fast rotation speed combined with a slow deposition rate ($<0.05 \text{ nm/s}$) can ensure that the composition of Pd and Co in the entire deposition region remains a constant.⁴⁸ However, due to the asymmetry configuration of the deposition sources, there are several important consequences that will affect the quality of the resulting Pd-Co alloy films. First, holes in the CHA_t have a truncated conical shape, as seen in Figure 1d and Figure S1. Second, near the edge of the holes, the fluxes of Pd and Co atoms cannot simultaneously reach the same region, causing poor alloy formation in these regions. Finally, the thickness of $Pd_{80}Co_{20}$ CHA_t is not uniform as the region between the nearest neighbor beads (Figure S2) experiences less deposition (see the line profiles in Figure 1d and Figure S1). This shadowing effect is more serious in the CHA_{300} as the diameter of the nanosphere is relatively large while the spacing between the nearest neighbor beads is relatively small. We note that the shadowing effect can be minimized by utilizing PS nanobeads with a smaller diameter or by reducing the incident angle. The average radius of the conical holes at the bottom glass side, r_b , can be extracted from Figure 1d and Figure S1 and shown in Table S1 with $r_{300} = 149 \text{ nm}$, $r_{450} = 125 \text{ nm}$, and $r_{600} = 98 \text{ nm}$. To further understand the nanomorphology and composition of the CHA nanostructures, scanning electron microscopy (SEM) imaging and energy-dispersive spectroscopy (EDS) elemental mapping were conducted using ultra-high-resolution SEM (SU-9000, Hitachi), as revealed in Figure 1c. An atomic ratio of Pd over Co of 77:23 is obtained and agrees well with the 80:20 ratio through deposition rate calibration. It is worth noting that the electron accumulation in the glass substrate negatively affects the contrast during SEM imaging. Nevertheless, the geometrical shape of the CHA_{450} is essentially the same to its AFM image in Figure 1b. The high-resolution SEM images of the CHA_{450} on a Si substrate with the same fabrication parameters are shown in Figure S3c,d.

In order to understand the crystalline property of the CHA_t , the X-ray diffraction (XRD) patterns were studied (Figure 2a). The AFM image and XRD diffraction spectrum of a CHA_∞ (thin film) are shown in Figure S3. All samples, regardless of RIE time, display a Bragg diffraction peak at 40.6° , which we assign to the (111) peak of the fcc $Pd_{80}Co_{20}$ alloy.^{50,51} The peak positions of the CHAs are slightly shifted to a higher angle than the (111) peak of pure Pd ($\sim 40.2^\circ$), which indicates that Co atoms are substitutionally incorporated into the Pd lattice.²³ The grain size of the $Pd_{80}Co_{20}$ nanocrystal, D_G , was estimated using⁵²

$$D_G = 0.9\lambda/\Delta_{2\theta}\cos\theta \quad (1)$$

where $\Delta_{2\theta}$ is the full width at half-maximum (FWHM) of the (111) Bragg peak at $2\theta = 40.6^\circ$ that can be extracted from fitting the patterns by a Gaussian function. We found that $D_G \sim 5.0$ nm for the CHA_{300} as shown in Table S2 and is significantly smaller than $D_G \sim 7.0$ nm observed in thin films of CHA_{600} and CHA_{450} . We hypothesize that this discrepancy is likely due to the larger shadowing effect in the CHA_{300} where the poor alloy formation nearby the edges of the structure causes a smaller effective grain size. From this, we can conclude that high-quality alloy formation in the CHA is relatively unchanged after enough RIE time, roughly above 450 s.

Figure 2b shows the current–voltage (I – V) characteristics of the sensors, whose resistance can be extracted by fitting the I – V s with a linear function as shown in the inset. The resistance of the device is inversely proportional to the radius of the holes or the intersection of the hexagonal resistance network. We calculated the elementary resistance of the network from first principles, based on the simplified geometry (see Section S2 for detailed calculations). The calculated resistance is summarized in Table S3 and plotted in the inset of Figure 2b. The calculated resistance closely matches the experimentally realized sensors, with the exception of CHA_{300} due to the aforementioned shadowing effects. As shown in Figure S3c,d, granules formed on top of the $\text{Pd}_{80}\text{Co}_{20}$ film might increase the scattering events of transport electrons at the interfaces and their tunneling between the grains causing larger resistivity in the thin film than the resistivity of the bulk material.⁵³ That might explain why the CHA_{300} with a slightly thinner effective thickness has a considerably larger resistance than that in the calculation (Figure 2b, inset).

The room-temperature electrical resistance of the CHA_i sensors in response to stepwise pulses of pure H_2 at ~ 10 mbar is shown in Figure 3a. The experimental setups for the hydrogen sensing characterization are described in Materials and Methods and Section S3. The response time of the device strongly depends on the radius of holes in the array, with the CHA_{450} sensor displaying the fastest sorption time upon

(de)hydrogenation. Generally, larger radii result in larger SVRs with corresponding faster response times (see Section S4 for detailed calculation of the SVR).⁵⁴ However, more serious shadowing effects can occur at larger hole radii, which may significantly reduce the effective SVR, and slow down the response times. In addition, the granules on top of the $\text{Pd}_{80}\text{Co}_{20}$ film might increase the SVR of the film and facilitate hydrogen absorption kinetics. In the CHA_i sensors, the absorbed hydrogen atoms at the interstitial sites behave as scattering centers for transport electrons in the electric current leading to an increase in the material resistance upon hydrogenation.³⁰ The resistance in the unit cell is significantly large at the bottleneck regions of the CHAs due to a smaller cross section (see Section S2). In addition, there are shorter diffusion paths to the nanostructure bulk in these bottleneck regions than other regions of the CHAs. Therefore, the response of the electric current in the sensor upon (de)-hydrogenation mainly relies on the hydrogen sorption kinetics at this bottleneck region. A simple scheme of the sensing mechanism can be seen in Figure S4c. For a thinner film of several-nm thickness, the resistivity of the film might be dominated by the resistance at the grain boundary.⁵³ Therefore, the expansion of the hydride grains upon the hydrogenation causes a better electric contact between the grains leading to a reduction in the resistance (see Figure S10c).⁵⁵ Since the effective thickness at the bottleneck regions of the CHA_{300} is ~ 6.7 nm (see Table S3), its resistance upon the hydrogenation might be influenced by both electron scattering with the hydrogen atoms and electron tunneling between grains. Such complex electron transport causes the reduction in the response time in the CHA_{300} in comparison to the CHA_{450} sensor. It should be noted that while the large SVR of the hole array structures is important for the sensing performance of both electrical sensors and optical sensors, the large material coverage and strong plasmonic property of the structures are necessary to obtain high-sensing performance in the optical sensors.^{43,44} In general, the sensitivity of the sensor device as a function of H_2 gas pressure is defined as

$$\frac{\Delta R}{R}(\%) = \frac{R(\text{H}_2) - R(0)}{R(0)}(\%) \quad (2)$$

where $R(\text{H}_2)$ and $R(0)$ are resistances of the device with and without H_2 gas, respectively. The commonly used response time, t_{80} , for the electric sensors is defined as the elapsed time from the baseline resistance to 80% of the saturation value, ΔR , and the release time t_{20} is defined as the elapsed time from the saturated resistance down by 80% of ΔR to the resistance that is equal to 20% of ΔR (see Figure 3a).³⁷ Notably, the sensitivity of the CHA_{450} sensor, $\Delta R/R$ (10 mbar) = 1.5%, with $t_{80} = 3.2$ s and $t_{20} = 21$ s, respectively.

Figure 3b shows the sensitivities of all four sensors plotted in a log-linear scale where the H_2 pressure varies 5 orders of magnitude, down to 10 μbar . In general, the isothermal sensitivities are relatively hysteresis-free, though some slight deviations between absorption and desorption may be observed and are attributed to the slight electric current drift in the device. The sensitivity is $\sim 7\%$ at 1 bar pressure, essentially the same for all CHA_i sensors. The sensitivity substantially decreases with decreasing H_2 pressure, P_{H_2} , analogously to Sieverts' power law at the thermodynamic equilibrium between H_2 molecules and dissolved hydrogen atoms, $P_{\text{H}_2} \propto (\Delta R/R)^n$, which predicts well the solubility of

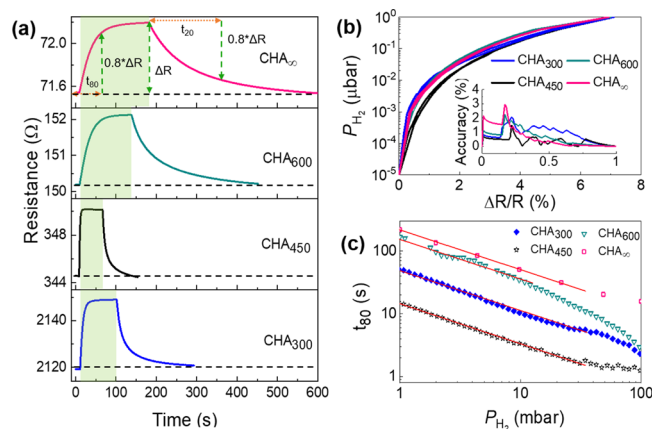


Figure 3. (a) Resistance response of each sensor in responding to pure hydrogen stepwise pulses (green areas) at ~ 10 mbar versus time at room temperature. The meaning of t_{80} and t_{20} response times along the time axis in the upper panel is demonstrated. (b) Sensitivity versus hydrogen gas pressure measured in vacuum mode. The inset shows the sensor accuracy. (c) Absorption time t_{80} of the sensor plotted in the log–log scale. The lines show a power-law fit in the low-pressure range.

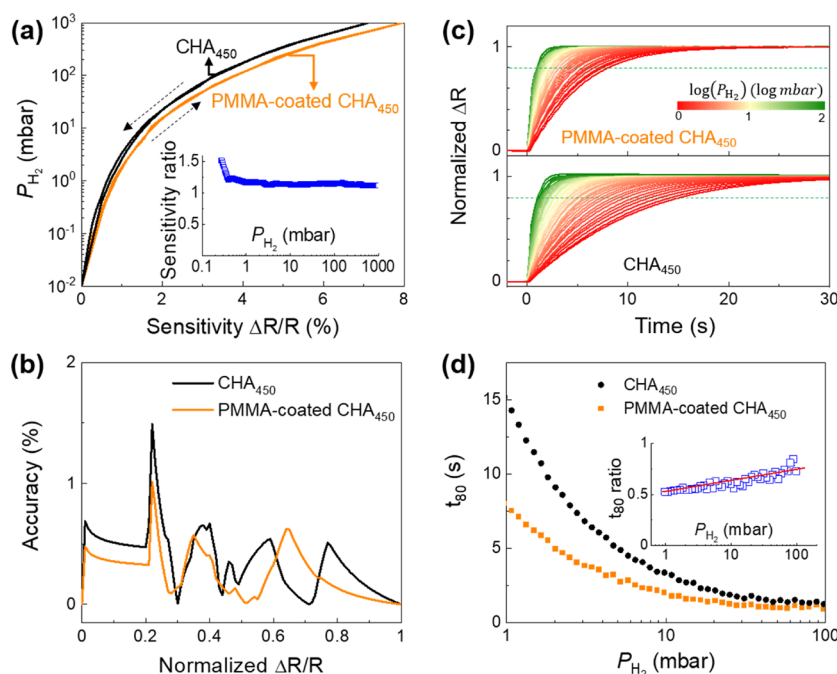


Figure 4. (a) Sensitivity of the PMMA-coated CHA₄₅₀ sensor in comparison to the CHA₄₅₀ sensor without PMMA measured at room temperature. The inset is the ratio of the sensitivity of the PMMA-coated sensor over the sensitivity of the sensor without PMMA. (b) Detection accuracy of each sensor. (c) Normalized resistance dynamics of two sensors in the absorption process. The color code indicates the resistance at pressure ranging from 1 to 100 mbar. (d) Response time t_{80} of the sensors extracted from panel (c). The inset shows the t_{80} ratio between the PMMA-coated sensor over the sensor without PMMA.

gases in metals ($n = 2$).^{56,57} Fitted parameters are shown in Figure S8a, and it was found that n_i is greater than 2 for all CHA_{*i*}, in agreement with the reported n by Hughes and Schubert.²⁷ $n_{450} = 2.86$ was found to be the largest, while the smallest $n_{300} = 2.13$ was very close to the gas solubility in a pure metal. We attribute the large n_{450} to the significantly large hydrogen permeability in alloys and surface-to-bulk-limited permeation at low temperature.^{20,21,56} Additionally, the larger n implies that the hydrogen embrittlement is less serious in the sensor due to the hydrogen-induced suppression of dislocation nucleation at the grain boundaries or free surfaces of the CHAs.^{25,26} We attribute the smaller n value of the CHA₃₀₀ sensor to the poor alloy formation as indicated by XRD and the possible island formation in the thin film as discussed in the previous paragraph.

A sensor's dependence on measurement history can be quantified in terms of "sensor accuracy", with the notion that the smaller the sensor accuracy value, the more precise the sensing readout (see Section S5 for details).¹⁵ The inset of Figure 3b shows the calculated accuracies of the CHA_{*i*} sensors, and the accuracy for all sensors in the P_{H_2} pressure range of 10 to 10⁶ μ bar is less than 3%, which surpassed the industrial requirements for H₂ gas sensing accuracy.² Remarkably, the accuracy is less than 1.5% across the tested pressure range for the CHA₄₅₀ sensors. Hysteresis contributes to poor sensor accuracy, and thus, the relatively hysteresis-free CHA sensors demonstrate high quality of accuracy across a wide pressure range. It is also worthwhile to note that in contrast to the optical study found by Wadell et al.,¹⁵ the accuracies of CHA sensors improve with increasing SVRs.

Figure 3c shows the t_{80} response times of the devices upon H₂ absorption plotted logarithmically in the 1–100 mbar range. All t_{80} –pressure responses follow a similar power law

dependence (with power value of ≈ -0.6) in the low-pressure range. Interestingly, the t_{80} value of the CHA₄₅₀ sensor is an order of magnitude faster than that of the CHA _{∞} . Similar to the CHA _{∞} thin film, a relatively slow response rate was also observed in Pd–Ni alloy thin films.²³ Overall, the CHA₄₅₀ device shows the best t_{80} response times at 100, 40 (flammable concentration), and 1 mbar with 1.2, 1.6, and 14 s, respectively. In general, an increased SVR results in a faster t_{80} response (with the exception of the CHA₃₀₀ sensor) (see Figure S9, for the detailed interpretation of t_{80} dependence on the SVR). We note that the enhancement of the SVR in the large hole size array can boost the resistive response time upon hydrogen's sorption, while poor alloy and grain boundary formation would shift the response time of the CHA_{*i*} toward the relatively slow response time of the pure Pd film. A similar trend for t_{20} can be seen in Figure S8b in which the response time t_{20} of the CHA₄₅₀ at 100, 40, and 1 mbar are 10, 13, and 52 s, respectively.

The composition and thickness of the Pd_{*x*}Co_{*y*} coating plays a crucial role in the resulting sensor properties. The sensors discussed thus far were fabricated with 15 nm nominal thickness of Pd₈₀Co₂₀ composition. To elucidate the effects of Co concentration, CHA₄₅₀ sensors composed of Pd₈₈Co₁₂ and Pd₉₀Co₁₀ with 15 nm nominal thickness were fabricated. The sensitivities of these Pd_{*x*}Co_{*y*} sensors as a function of P_{H_2} are shown in Figure S10a,b. On the other hand, the positive sensitivity of the sensor is increased with increasing Pd concentration, and the response time suffers seriously due to decreased hydrogen permeability and lattice imperfections.^{22,23,58} Thus, 20% Co offers the best tradeoff between sensitivity and response time of the alloys tested. To elucidate the effects of thickness, CHA₄₅₀ sensors composed of Pd₈₀Co₂₀ were fabricated at thicknesses of ~ 3.5 and ~ 6.0 nm (5 and 10

nm nominal thicknesses, respectively) in order to modify the SVR. Their resistances are significantly larger than the calculated resistances using first-principles calculation (e.g., 50 Mohms for the 3.5 nm-thick sensor as shown in Figure S10c). Axelevitch et al. found that at lower thicknesses than 10 nm, the metal coating favorably forms islands on the glass substrate with low inter-island conductivity.⁵⁹ Therefore, the conductivity of the CHA₄₅₀ at these thicknesses is governed by the low conductivity at the grain boundary. The sensitivity and response time of the 3.5 nm-thick Pd₈₀Co₂₀ sensor as a function of P_{H_2} are shown in Figure S10c,d. Interestingly, these CHA₄₅₀ sensors have negative (instead of positive) and higher magnitude sensitivities, yet slower response times. When exposed to H₂, the islands expand causing a better electrical connection to the adjacent islands resulting in an increase of the electrical conductivity.⁵⁵ The slower response is obviously due to slow mechanical expansion of the Pd₈₀Co₂₀ islands that are pinned on the glass substrate. The response time t_{80} of the sensors in Figure S10d is significantly larger than that of the CHA₄₅₀ sensor as presented in Figure 3c.

Highly chemical-resistant and hydrophobicity polymers such as PMMA and Teflon have been proven to effectively filter poisonous gases.^{19,40,60–64} Notably, these polymers have also been found to significantly improve the H₂ storage capacity, detection sensitivity, and response time.¹⁹ By analyzing the sorption kinetics, it has been found that the improvement of the sensing performance due to polymer coating is associated with the large reduction of the apparent sorption energy barrier for surface-to-subsurface hydrogen diffusion when the hydrides are covered and bonded with the coating polymers according to Nugroho et al.¹⁹ Thus, the optimized CHA₄₅₀ sensors were coated by ~200 nm PMMA followed by annealing at 160 °C in N₂ for 30 min. The PMMA coating did not modify the electrical properties of the CHA₄₅₀ sensor, as observed in the characteristic I – V plots shown in Figure S11a. Figure 4a shows the hysteresis-free sensitivity of the PMMA-coated CHA₄₅₀ sensor in comparison to the sensor without PMMA coating in H₂ pressures ranging from 10 to 10⁶ μ bar. The sensitivity of the PMMA-coated CHA₄₅₀ sensor is greatly improved at all measured P_{H_2} .¹⁹ The enhancement factor, the ratio of the sensitivity of the sensor with PMMA to the sensitivity without PMMA, increases as P_{H_2} decreases by nearly 60% at 0.3 mbar pressures as shown in the inset. Therefore, these PMMA-coated sensors are also favorable for measuring extremely low concentrations of H₂. Additionally, the detection accuracy of the PMMA-coated sensor is significantly enhanced, with all measurements having an uncertainty of less than 1% (Figure 4b). It is worthwhile to note that the increased sensitivities of polymer-coated nanosensors were previously attributed to the red-shifting of plasmonic resonances in an optical detection scheme.¹⁹ However, this mechanism clearly cannot be responsible for the effects seen in the electrical detection scheme presented here. A more general and plausible explanation is that the polymer coating modifies the properties of the subsurface layer containing higher energy absorption sites, which reduces the enthalpy of absorption and consequently increases the solubility at a specific hydrogen partial pressure.^{65,66} Modification of subsurface site properties is also consistent with the increased kinetics observed for the PMMA-coated samples, as described below.

The upper panel of Figure 4c displays the normalized resistance dynamics of the PMMA-coated CHA₄₅₀ sensor

exposed to different H₂ gas pressures. Generally, the response time is much faster than equivalent CHA₄₅₀ sensors without PMMA, shown in the lower panel. A detailed comparison of t_{80} response times in coated and uncoated sensors is plotted in Figure 4d. We highlight the extremely low response time of the PMMA-coated CHA₄₅₀ sensor at 100, 40 (lower flammable limit concentration), and 1 mbar: the t_{80} are values 0.9, 1.0, and 7.5 s, respectively. A similar trend was found for the desorption time (t_{20}) (Figure S11b,c), in which the t_{20} response times of the CHA₄₅₀ at 100, 40, and 1 mbar are 6.1, 8.5, and 34 s, respectively. The t_{90} and t_{10} values of the CHA₄₅₀ versus H₂ pressure are analyzed and shown in Figure S11d. The extremely low level detection performance of the CHA₄₅₀ sensors before and after PMMA coating was measured in stepwise pressure pulses of pure H₂ in the vacuum mode from 5000 to 11 μ bar at a 1.25 Hz sampling rate (Figure 5a).

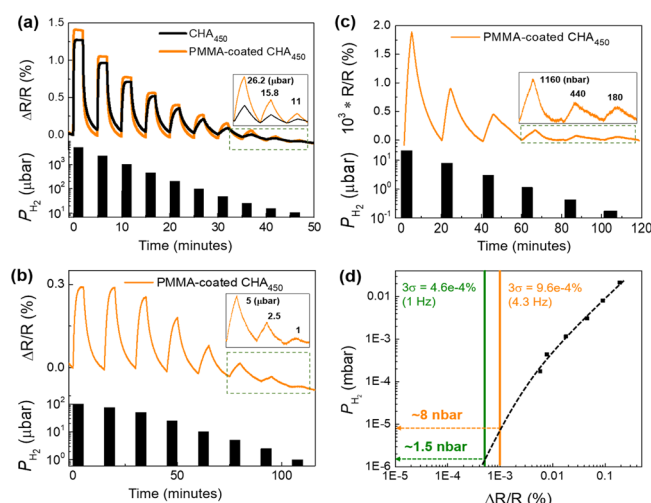


Figure 5. (a) Limits of detection (LODs) of CHA₄₅₀ and PMMA-coated CHA₄₅₀ sensors react with stepwise pulses with different pure hydrogen gas pressures in the vacuum mode at room temperature. (b) LOD of PMMA-coated CHA₄₅₀ reacts with stepwise hydrogen gas concentration below 100 ppm in a N₂ host gas using a gas blender at 1 atm. (c) LOD PMMA-coated CHA₄₅₀ sensors react with stepwise pulses with different H₂ mixed gas pressures (4% H₂ balance in N₂) in the vacuum mode at room temperature. Insets in panels (a) and (c) show zoom-in features at the low hydrogen pressure range. (d) Measured $\Delta R/R$ as a function of H₂ pressure derived from panel (c). Black dashed lines show extrapolation from the lowest reliably attainable data point in our system to the 3 σ point, indicating LODs <10 ppb and <2 ppb for sampling frequencies of 4.3 and 1 Hz, respectively. The orange and green lines mark the extrapolated LOD at 3 σ for the 4.3 and 1 Hz sampling frequencies, respectively.

Notably, both CHA₄₅₀ and PMMA-coated CHA₄₅₀ can resolve even the lowest measured pulse and can potentially provide detection at even lower H₂ pressures (~ 4 μ bar is the low pressure limit of our gas cell setup). The sensitivity of the PMMA-coated CHA₄₅₀ sensor clearly shows a factor of about 2.5, better than that in the corresponding CHA₄₅₀ in this extremely low level pressure regime (Figure 5a, inset) which is in agreement with the sensitivity ratio trend shown in the inset of Figure 4a. Further confirming the sensing capabilities of the CHA sensors, the PMMA-coated CHA₄₅₀ sensors were exposed to H₂ in flow mode with stepwise H₂ gas pulses having concentrations (C_{H_2}) from 100 (or 100 ppm H₂) to 1 μ bar (or 1 ppm H₂) with N₂ as the balance to maintain

atmospheric pressure (Figure 5b). The N_2 gas is usually used as a carrier gas since it has a negligible effect on the hydride sensing performance. Remarkably, distinct sensor responses can be detected at the H_2 concentration as low as 1 ppm with high signal-to-noise ratios (Figure 5b, inset). In order to further explore the ultimate LOD of the CHA sensor and overcome the low pressure limit of our gas cell setup ($\sim 4 \mu\text{bar}$), a 4% H_2 mixed gas in balance N_2 rather than pure H_2 gas was used. Figure 5c shows the sensitivity of the PMMA-coated CHA_{450} sensor in stepwise pressure pulses of the H_2 mixed gas in the vacuum mode from 540 to $4.4 \mu\text{bar}$ at a 4.3 Hz sampling frequency. This is corresponding to the pure H_2 pressure from 21.6 to $0.176 \mu\text{bar}$. The inset is the zoom-in feature at the low H_2 pressure range where the detection sensitivity at $0.176 \mu\text{bar}$ is well-defined. The ultimate LOD can be calculated using the data extrapolation method.¹⁹ The measured sensitivity as a function of pure H_2 pressure derived from attainable data points in our system to the 3σ point indicates record-low LODs of ~ 8.0 (equivalent to ~ 8.0 ppb H_2) and ~ 1.5 nbar (equivalent to ~ 1.5 ppb H_2) of pure H_2 pressure for sampling frequencies of 4.3 and 1 Hz, respectively (see Figure S12, Supporting Information for details of calculating the standard deviation, and σ is the signal noise).

The inertness tests of the CHA_{450} sensor sensitivity (before and after PMMA coating) against the CO, synthetic air, and H_2O gas interference are shown in Figure 6a,b. Those gases cause serious effects on the sensing performance of the Pd-Co optical sensor.⁴⁴ In Figure 6a, the first three stepwise gas pulses of 4% H_2 in N_2 balance were applied followed by three pulses of 4% H_2 and 0.15% CO in N_2 balance and three pulses of 4% H_2 in N_2 balance again. While the CHA_{450} without the protecting PMMA membrane shows slight reduction of the

sensitivity by $\sim 7\%$, the sensitivity of the PMMA-coated CHA_{450} is absolutely inert to the presence of the CO gas with 0.15% concentration. In addition, the response and release time of the PMMA-coated CHA_{450} are almost unchanged in comparison to a slight change in the pristine CHA_{450} . The results clearly confirm the unique functionality of the PMMA membrane in filtrating the poisonous gases as such CO gas.

For the oxygen and humidity effects, we have designed and carried out the tests in synthetic air carrier gas with percentages of humidity of 0, 40, and 90%. Figure 6b shows the sensitivity of the PMMA-coated CHA_{450} sensor in different carrier gases including N_2 and synthetic air with 0 and 40% of humidity while a hydrogen gas content of 2% is introduced into the different carrier gases using the flow mode setup (see Figure S13 for extended cycle tests). The oxygen in the synthetic air increases the sensitivity from 1.39 ± 0.05 (2% H_2 in N_2) to $1.51 \pm 0.05\%$. The treatment in air at room temperature has been experimentally shown to enhance H_2 permeability for Pd-based membranes leading to an enhancement in the sensitivity measurement.⁶⁷ Two hypotheses have been proposed to explain the enhancement based on the surface cleaning effect and microstructure change (surface area increase) effect.⁶⁷ The sensitivity of the sensor essentially remains the same throughout the cycle tests. For 40% of humidity in the synthetic air, the sensitivity reduces to $1.32 \pm 0.05\%$ and a slight effect on the response time was observed. The response times and sensitivity are seriously affected when the device is operated in the synthetic air with 90% of humidity (Figure S14). These effects of humidity on the sensor performance are readily understood.⁶⁸ When the water molecules are in contact and dissociatively adsorbed on the Pd-surface, they form OH molecules with the assistance of surface chemisorbed atomic oxygen. The OH molecules can react with the adsorbed atomic hydrogens to form the gas-phase water, thus affecting the hydrogen absorption kinetics of the hydrides.⁶⁸ The humidity effect on the sensor suggests that the PMMA coating layer does not effectively prevent the H_2O molecules from penetrating through it, especially when the moisture concentration is high.

In order to examine the short- and long-term stability of PMMA-coated CHA_{450} sensors, the sensor was aged in industrial-grade nitrogen (0.1 ppm O_2 and H_2O) or air (with $\sim 50\%$ moisture). The sensitivity after exposure to industrial-grade nitrogen for 2 and 11 months was tested using stepwise pressure pulses of 4% H_2 in N_2 at a 1 atm mixture. The average sensitivity of 10 consecutive pulses after 2 months was $2.29 \pm 0.02\%$, identical to the sensitivity before aging (Figure S15a). However, there is a reduction of $\sim 4\%$ in the sensitivity after 11 months in N_2 gas (Figure S15b, upper panel). When the sensor was exposed to the air, its sensitivity increased gradually and stabilized after 2 weeks with an average sensitivity of $(2.55 \pm 0.02)\%$ (Figure 6c, black circles in the upper panel). After that, we observed a negligible change of the sensitivity and response time for the sample aged in air (Figure 6c, red lines in the upper panel). In particular, the H_2 sensitivity was $(2.57 \pm 0.02)\%$ after 2 more months in air, highlighting the good stability of these sensors after the initial 2 weeks of preconditioning.

As the $Pd_{80}Co_{20}$ alloy is magnetic, it would be expected that the sensing performance might be affected by an external magnetic field. The lower panel in Figure 6c shows the effect of a 3.2 kOe constant field with a parallel field direction with the electric current on the sensitivity dynamics of PMMA-coated

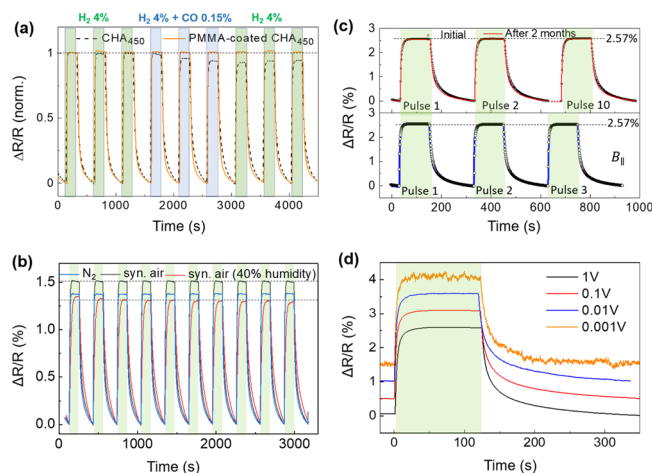


Figure 6. (a) Inertness tests of CHA_{450} sensor sensitivity against the CO interference. The sensitivities are normalized to one at the first stepwise pulses. (b) The humidity tests of PMMA-coated CHA_{450} with gas pulses of 2% H_2 in N_2 (blue line), synthetic air with 0% (black line), and 40% (red line) of humidity. (c) Short-term repeatability (open circles in the upper panel) and long-term stability (red lines) of the PMMA-coated CHA_{450} sensor stored in air for 2 months with 10 stepwise gas pulses with 4% H_2 in N_2 at 1 atm (only pulses 1, 2, and 10 are presented). In the lower panel, the repeatability of the sensor when experiencing a parallel magnetic field with the applied electric current (blue line at $B_{||} = 3.2$ kOe). The open circles are the sensitivities without the field for comparison. (d) Sensor performance under different driving voltages. The responses are shifted for clarity.

CHA₄₅₀ sensors in response to several stepwise pressure pulses of 4% H₂ in N₂ at 1 atm. Clearly, there is no change in the sensitivity and response time of the sensor before (open circles) and after (solid line) applying the magnetic field. Similar results for the perpendicular field can be seen in Figure S15b. Typical hysteresis loops from the anisotropic magneto-resistance (AMR) for both magnetic field directions scanning between +3.2 and −3.2 kOe are presented in Figure S16. For the out-of-plane field, the AMR reaches nearly −0.1% without H₂ gas and −0.12% with H₂ gas when the maximum field is applied (Figure S16a). For the in-plane field, however, the AMR changes its sign from +0.045% without H₂ gas to −0.01% with H₂ gas (Figure S16b). This AMR reversal is attributed to the substantial change in the sensor magnetic property upon hydrogenation. The underlying mechanism for the AMR reversal should be further investigated but is not the scope of this report. Since the maximum change of the sensitivity of the sensors in response to the 3.2 kOe field at any direction is negligible, the sensors are able to operate precisely in a moderate field regardless of its direction.

Sparking from electrical devices is a concern in potentially flammable environments, such as those containing H₂.⁶⁹ In order to reduce the risk of sparking from electric discharge and joule heating released from the sensor,^{3,5} CHA₄₅₀ sensor performance was measured from 1 mV to 1 V. As shown in Figure 6d and Figure S15c, there is no obvious change in sensor performance when the joule heating is increased by 6 orders of magnitude. The electric field insensitivity of the CHA sensors is in direct contrast to other comparable sensors, such as those based on transistors or Schottky junctions.^{6,7} Remarkably, the extremely low power consumption in the device operating at 1 mV applied voltage is ~2 nW.

CONCLUSIONS

In conclusion, we obtained a new standard in H₂ sensing performance at room temperature by demonstrating a measurement range spanning 8 orders of magnitude, an LOD of <10 ppb, high accuracy of less than 1% in the 10–10⁵ μ bar range, extremely low power consumption in the order of nW, and $t_{80} \approx 1.0$ s (7.5 s) at 40 mbar (1 mbar) in a single nanoscale sensor. The PMMA-coated CHA₄₅₀ system, which is a nanoscale resistance network, is among the fastest and most sensitive electric H₂ sensors ever reported while also maintaining long-term environmental stability and inertness against poisonous gases such as CO and O₂ (see Table S4).^{15,18,70} However, high humidity concentration in synthetic air has a serious effect on the sensing performance of the nanosensor. The sensor performance is insensitive to operation voltage/current and applied magnetic field, a crucial performance metric for demanding applications such as leak detection and concentration control. However, there are further opportunities for improving the CHA nanosensors. For example, the demonstrated sensing platform can be further improved by suppressing the shadowing effect with a smaller diameter precursor, by reducing the incident angles of the atomic fluxes to the substrate, or by decreasing the film thickness.⁴⁴ The CHAs enable a noncontact fine modulation of the hydrogen (de)sorption signal by a small alternative applied magnetic field via the AMR effect, which is important for noise reduction and obtaining a higher LOD. We also believe that even more effective and efficient sensors can be developed with further understanding of the molecular sieving effects of the polymeric layers, the interfacial coupling of the polymer and

metal, and how these cooperatively improve sensor performance.

MATERIALS AND METHODS

Materials. PS nanospheres (Polysciences Inc., $D = 500 \pm 10$ nm) and ethanol (Sigma-Aldrich, 98%) were used to create the nanosphere monolayers. Palladium (99.95%) and cobalt (99.95%) from Kurt. J. Lesker Company were utilized for electron beam deposition. Deionized water (18 M Ω cm) was used for all experiments.

Nanohole Array Fabrication. The nanofabrication started with growing hexagonal close-packed nanosphere monolayers on glass substrates (1 $\times$ 1 cm²), which were prepared by an air/water interface method.^{42,43,47} The nanosphere diameter $D = 500$ nm was chosen since the monolayers can have the highest quality with this size. The RIE with different etching times of 300, 450, and 600 s was used to reduce the bead size resulting in different monolayer templates used as shadow masks for electron beam deposition. The substrates were co-deposited by Pd and Co sources under a total rate of 0.05 nm/s yielding a thin Pd₈₀Co₂₀ alloy film with different thicknesses of 5, 10, and 15 nm. To increase the mixing uniformity between Pd and Co, the sample holder was rotated azimuthally with a constant rotation rate of 30 rpm during the deposition process. The substrate was then cut into a standard rectangular size of 5 $\times$ 10 mm² followed by monolayer liftoff by using a Scotch tape technique. Electronic contacts were implemented on the device by indium soldering. In some cases, the device was covered by a PMMA film prepared by solution spin-casting. First, PMMA pellets were fully dissolved in toluene to obtain a 20 mg/mL solution concentration. The solution then was spin-cast with a speed of 2000 rpm to get an approximate 200 nm thickness of PMMA on top of the Pd-Co alloy hole array.

Nanomorphology and Composition Characterization. The nanomorphologies of fabricated samples were measured by an atomic force microscope (AFM, Park NX10), and all the AFM images were analyzed using XEI - Image Processing and Analysis Software. For the X-ray pattern, we used a Cu K α X-ray machine with $\lambda = 0.154$ nm. For obtaining the various Bragg bands from the alloy nanocrystalline grains, we removed the scattering pattern of the substrate. The nanocrystalline grain size D was estimated using the Scherrer's equation.⁵² Scanning electron microscopy (SEM) was performed with a Thermo Fisher Scientific (FEI) Teneo field emission scanning electron microscope (FESEM). Energy-dispersive spectroscopy (EDS) elemental mapping was performed with a 150 mm Oxford XMaxN detector. Ultra-high-resolution SEM was performed with a SU-9000 Hitachi (with a resolution of 0.4 nm at 30 kV).

Resistance Measurement. The resistance of the nanoscale CHAs was measured in a vacuum mode by the multimeter Keithley 2400 source in a constant voltage mode. The sample was positioned in a home-built H₂ gas cell where the pressure of H₂ gas was measured by several vacuum gauges at different pressure ranges.⁴³ The H₂ gas pressure was monitored by three independent pressure transducers with different ranges, which cover the pressure range of 10^{−6} to 1.1 bar (two PX409-USBH, Omega and a Baratron, MKS). The electric response/release time measurements were performed at 4.3 Hz sampling frequency. In addition to the vacuum mode, the LOD measurement was also performed in flow mode, which has a lower limit of H₂ gas concentration by orders of magnitude depending on the use of H₂ mixed gas. 100 ppm H₂ in nitrogen mixture gases (Airgas) was diluted with ultra-high-purity nitrogen gas from Airgas to targeted concentrations by a commercial gas blender (GB-103, MCQ Instruments). The gas flow rate was kept constant at 400 mL/min at 1 atm for all measurements. All experiments were performed at 25 $^{\circ}$ C.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnm.1c00169>.

Morphology study of composite hole arrays; CHA resistance calculation; hydrogen gas sensing character-

ization setups; calculated surface-to-value ratio (SVR) based on the effective hole radius and effective thickness; sensor accuracy calculations; sensor performance and modeling; and sensor stability (PDF)

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Notes

The authors declare no competing financial interest.

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