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Journal

Sensors and Actuators B Chemical, 444

ISSN

0925-4005

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Publication Date

2025-12-01

DOI

10.1016/j.snb.2025.138335

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Mitigating humidity interference in chemiresistive hydrogen sensors through hydrophobic surface functionalization

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ARTICLE INFO

Keywords:

Chemiresistive gas sensors
Surface functionalization
Hydrogen sensors
Humidity tolerance
Tin oxide
Hexamethyldisilazane

ABSTRACT

Chemiresistive gas sensors based on semiconductor metal oxides, such as tin dioxide (SnO₂), are indispensable for detecting and monitoring toxic gases and pollutants, making them critical components in industrial and environmental applications. To enhance their performance, the metal oxides are loaded with noble metals such as palladium (Pd). However, ambient humidity poses a significant challenge to their performance. The presence of adsorbed water molecules on the oxide surface can considerably impair sensor sensitivity and overall performance. To address this issue, in this paper, we report on the application of an ultrathin, hydrophobic layer of hexamethyldisilazane to the surface of a Pd/SnO₂ sensor. This study investigates the influence of hydrophobic surface modifications on the metal oxide interface, focusing on their impact on sensor sensitivity and selectivity. The resulting sensor exhibits superior hydrogen sensing capabilities, operating effectively at low temperatures even in high humidity environments. Furthermore, the hydrophobic modification reduces the sensor's susceptibility to interfering gases, thus enhancing its selectivity. The combined enhancements in moisture resistance and selectivity achieved through HMDS surface modification, along with the superior sensitivity of Pd/SnO₂ sensors, facilitate the development of gas sensors with enhanced humidity tolerance and broader applications.

1. Introduction

Gas sensors are devices designed to detect the presence and concentration of specific gases in the environment. Their fundamental operational principle involves converting the chemical interaction between gas molecules and the sensor surface into an electrical signal[1]. In recent years, semiconducting metal oxides (SMOX)-based gas sensing technologies have garnered considerable attention due to several advantages such as their compact size, low cost, maintenance-free operation, and ease of production[2–4]. As the hydrogen economy continues to grow, the detection of hydrogen has become a pivotal aspect of scientific research[5–7]. This growing demand is driven by the increasing need for efficient monitoring and management of hydrogen production, storage, and usage. In various fields such as energy solutions, environmental monitoring, industrial safety, and aerospace, hydrogen sensors

play an essential role. Their ability to ensure safety and drive technological advancements across these sectors underpins their growing significance[8–10].

Despite the sustained expansion in the number of applications and market demand for sensors for various gases, several challenges remain to be addressed. In general, semiconductor-based gas sensors demonstrate insufficient sensitivity and selectivity[11]. It has been demonstrated that increasing operating temperature can improve their sensitivity. This is because sufficient energy is needed to facilitate the reaction between the gas molecules and those adsorbed on the semiconductor surface[12,13]. In addition, it has been demonstrated that the functionalization of surfaces with noble metals such as Pd and Pt can enhance sensor performance, including reducing the operating temperature. However, a significant issue persists with semiconductor-based gas sensors as their detection capability is

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influenced by ambient humidity. This phenomenon can be attributed to the interaction of ambient water vapor with the sensor surface. Increased humidity leads to competition between water and target gas molecules for active sites on the sensor surface. This results in inaccuracies and a reduction in the sensor's sensitivity to target gases[14].

To address these challenges, several anti-humidity strategies have been developed to improve sensor performance and reliability[15–17]. Physical isolation by polymeric membranes is one of the techniques used to protect the sensor from moisture[15]. However, this can complicate the packaging process and potentially result in an increase in the overall size and weight of the sensor. Another approach is high-temperature heating, which involves maintaining the sensor at an elevated temperature to mitigate the effects of moisture[18]. This is due to the fact that the rise in temperature effectively causes water molecules to desorb from the sensor surface[19,20]. Nevertheless, prolonged high-temperature operation can result in performance degradation in semiconductor-based sensors, including material aging, thermal stability issues, and increased operating costs[21,22]. Surface modification with a hydrophobic coating serves as an effective strategy to address this issue. The application of hydrophobic coatings results in reduction in the surface energy of the sensor, which in turn diminishes its affinity for water molecules[23–27]. This approach enables gas sensors to exhibit more consistent gas detection performance by minimizing the influence of humidity, thereby enhancing their reliability and accuracy in practical applications. However, applying a thicker coating can alter the sensor's baseline resistance and hinder gas diffusion, particularly the diffusion of gaseous O_2 into the inner SnO_2 layer, which may compromise the sensor's sensitivity[28].

In this study, atomically dispersed catalyst Pd on SnO_2 (referred to as ADC Pd/ SnO_2), in which Pd atoms are stabilized on a SnO_2 nanoparticles in the form of single atoms and small Pd nanoclusters, are synthesized using a wet impregnation method[29] and subsequently modified through vapor-phase deposition of hexamethyldisilazane (HMDS). This approach integrates two distinct strategies to optimize the gas sensor surface for enhanced performance. First, studies have shown that functionalizing metal oxides with noble metals can markedly improve the performance of gas sensors at lower operating temperatures, effectively lowering the temperature threshold for efficient semiconductor-based gas sensing. This is due to the high catalytic activity of noble metals such as platinum and palladium (Pd), which facilitates the activation of gas molecules. Among these, palladium is widely employed in advanced hydrogen sensing applications due to its particularly efficient sensing properties, high selectivity for hydrogen, and ability to operate at low temperatures[30,31]. More uniquely, integrating individual Pd atoms with small clusters onto SnO_2 significantly increases the catalytic activity and selectivity toward hydrogen compared to larger nanoparticles. For these reasons, ADC Pd/ SnO_2 is selected as the sensing material. Secondly, HMDS, an organosilicon compound with the molecular formula $[(CH_3)_3Si]_2NH$, has been shown to form a monolayer on oxide surfaces, rendering them hydrophobic[32–34]. Here, the successful coating of hydrophobic trimethylsilyl $(CH_3)_3Si$ groups onto SnO_2 surface via vapor-phase deposition is demonstrated, providing a nonpolar, water-repellent surface. The resulting sensor exhibits exemplary hydrogen sensing capabilities across a broad range of relative humidities (RH).

2. Experimental methods

2.1. Chemicals

Palladium (II) acetate $(Pd(OAc)_2$, 98 %), toluene (99.8 %, anhydrous) and hexane (≥ 95 %) were supplied by Sigma-Aldrich. Tin (IV) oxide nanopowder (99.9 %) was purchased from Inframat® Advanced Materials. Ethanol (≥ 99.9 %), isopropyl alcohol (99.9 %) and acetone (≥ 99 %) were acquired from Merck Millipore. All aqueous solutions were prepared using Milli-Q® ultrapure water with a resistivity of 18.2

$M\Omega\cdot cm$.

2.2. Materials synthesis

Atomically dispersed Pd/ SnO_2 catalysts were synthesized via a wet impregnation method at room temperature, where the nominal loading by weight of Pd to SnO_2 was 0.75 wt%[29]. Specifically, 7.97 mg of palladium(II) acetate $[Pd(OAc)_2]$, serving as the Pd precursor, was dissolved in 15 mL of anhydrous toluene under an inert atmosphere to form a clear solution. Subsequently, 0.5 g of phase-pure tin(IV) oxide (SnO_2) nanopowder (99.9 % purity) was added to the $Pd(OAc)_2$ solution, and the mixture was stirred at 25°C overnight under an inert atmosphere. The resulting Pd/ SnO_2 catalyst was separated by centrifugation and washed three times with anhydrous toluene. The sample was then dried under dynamic vacuum at 25°C overnight and annealed in ambient air at 325°C to remove ligands from the metal sites. The annealing protocol involved a 90-min ramp to 325°C, followed by 180 min at 325°C, and a 75-min cooling period.

To investigate the interaction between HMDS and SnO_2 , 30 nm-thick SnO_2 thin films were deposited via atomic layer deposition (ALD) using Tetrakis(dimethylamino)tin(IV) as the Sn precursor and O_2 as the oxidant. The deposition was carried out using the Oxford FlexAl ALD system (Oxford Instruments, Oxfordshire, UK) at 300°C, with plasma treatment incorporated into the process. The dose times for the Sn precursor and O_2 plasma were set at 500 ms and 5 s, respectively, with a purge time of 5 s for each step. The deposition rate was approximately 1 Å per cycle.

2.3. Characterization methods

XPS measurements were performed on an Omicron Dar400 system with an achromatic Al K α X-ray source. Contact angle measurements were conducted using an optical tensiometer (Ramé-Hart Instrument Co., Model 290) with the pendant drop method. A standardized 1 μL drop of deionized water was applied to the surface of each sample, and the contact angle was measured using DROPimage software for surface energy and tension analysis.

High-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) measurements were conducted using an image-corrected FEI ThemIS microscope at an accelerating voltage of 300 kV. The experiments were performed at the National Center for Electron Microscopy (NCEM) of the Molecular Foundry (MF), Lawrence Berkeley National Laboratory (LBNL).

2.4. Sensor fabrication and testing

The HMDS-modified ADC Pd/ SnO_2 sensor fabrication is illustrated in Fig. 1(a). First, a prepared colloidal nanoparticle solution was drop-cast onto a Micrux glass substrate containing thin-film Ti/Pt interdigitated electrodes (IDE). After pre-cleaning the IDE, 2.5 μL of ink containing nanoparticles dispersed in ethanol at a 5 wt% concentration was drop-cast onto the IDE. The IDE was first heated to 50°C to facilitate uniform coverage during the casting process and then annealed at 275°C. The annealing procedure involved ramping up to 275°C over 1 h and 15 min, holding at 275°C for 3 h, and cooling to room temperature in 50 min. A photograph of the final sensor is presented in Fig. 1(b).

To modify the ADC Pd/ SnO_2 surface and render it hydrophobic, the sensor was treated with vapor-phase HMDS. The sensor, with its electrode pads protected with Kapton tape, was placed in a smaller beaker, which was then positioned inside a larger beaker containing 10 mL of liquid HMDS. The larger beaker was tightly sealed and heated to 100 °C in an oven for 5 h. During this treatment, HMDS vapor adsorbed onto the sensor surface and reacted with the hydrophilic hydroxyl groups, resulting in a hydrophobic surface due to the terminal $-CH_3$ groups. This surface modification process was monitored by time-dependent contact angle measurements, which confirmed a progressive increase in

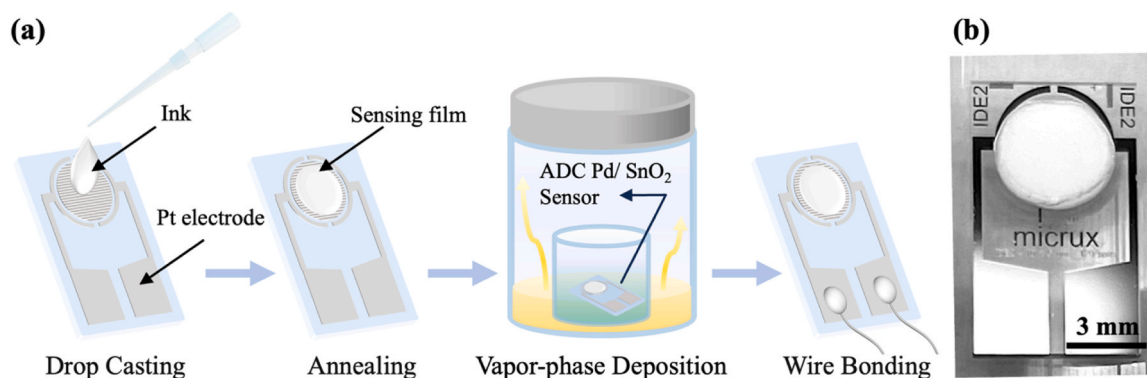


Fig. 1. (a) Schematic illustration of the HMDS-modified ADC Pd/SnO₂ sensor fabrication, including drop-casting the colloidal nanoparticle solution onto a Au IDE on glass substrate, annealing, vapor-phase HMDS deposition, and wire bonding. (b) Photograph of the HMDS-modified ADC Pd/SnO₂ sensor.

hydrophobicity until saturation was reached, as shown in Figure S1. Through this relatively low-temperature vapor-phase method, self-assembled monolayers of HMDS were formed on the SnO₂ surface, providing a consistent and uniform hydrophobic coating [35]. The successful deposition of the HMDS layer on SnO₂ was further confirmed by field emission scanning electron microscopy (FESEM) imaging, as shown in Figure S2.

For gas sensing measurements, a computer-controlled gas delivery system was used to introduce sample gases into the chamber. Hydrogen (H₂) was the primary target gas, supplied from a cylinder containing 4.091 % H₂ in Ar (Airgas). For selectivity tests, the sensor responses to additional target gases, including CO (Airgas, 1000 ppm in air), CH₂O (Airgas, 20 ppm in N₂), NH₃ (Airgas, 1000 ppm in N₂), CO₂ (Airgas, 53,800 ppm in N₂), CH₄ (Airgas, 50,000 ppm in N₂), and C₅H₁₂ (Airgas, 5000 ppm in N₂), were studied. Further details on the sensor setup, gas sensing chamber, testing conditions, and measurement procedure can be

found in the Supporting Information (Figure S3).

3. Results and discussion

3.1. Materials characterization

The synthesized catalyst was thoroughly characterized using various physical techniques. FESEM analysis, shown in Fig. 2(a), reveals that the ADC Pd/SnO₂ forms polycrystalline aggregates of polydisperse SnO₂ nanoparticles with a broad size distribution up to approximately 200 nm. High-resolution transmission electron microscopy (HRTEM) images in Fig. 2(b) demonstrate well-dispersed spherical Pd nanoclusters of approximately 2 nm on the highly ordered SnO₂ surface. The interface between the Pd nanoclusters and the SnO₂ nanoparticles is clearly visible. The distinctive interplanar crystal spacings observed between the Pd nanoclusters and the SnO₂ nanoparticles confirm their

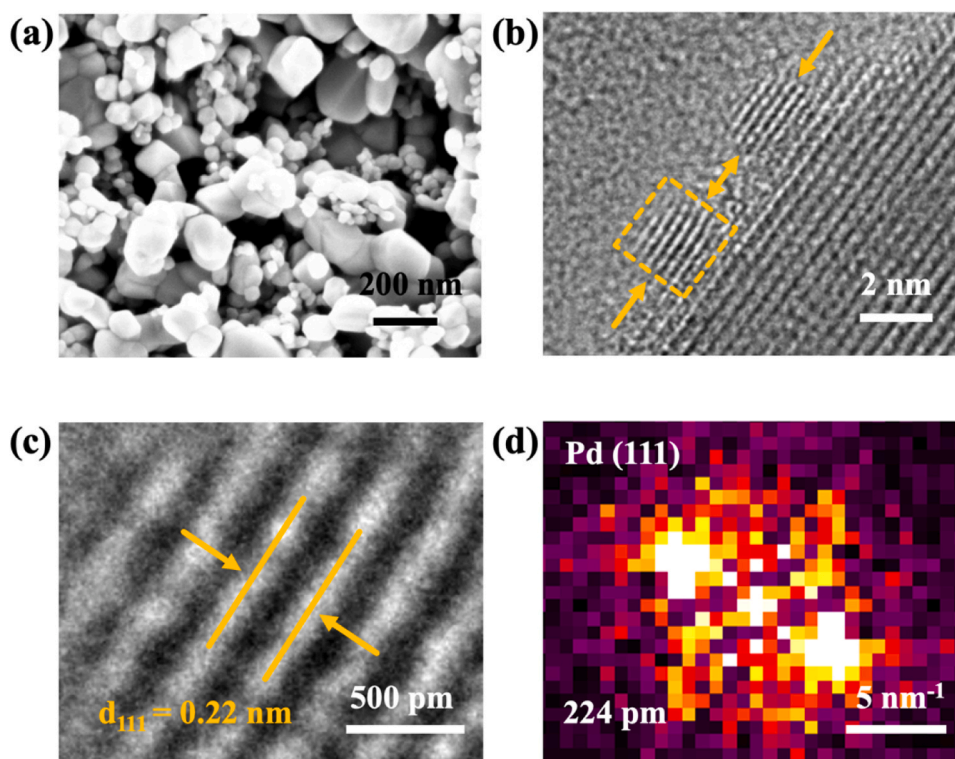


Fig. 2. (a) FESEM image of ADC Pd/SnO₂. (b) HRTEM image showing the interface between the Pd nanocluster (indicated by the arrows) and the SnO₂ nanoparticle surface (in the lower-right region of the image). (c) Magnified view of Pd nanocluster highlighted in (b), showing its (111) plane. (d) The corresponding FFT pattern of (c).

differing elemental composition. A magnified view in Fig. 2(c) with the corresponding fast Fourier transform (FFT) pattern in Fig. 2(d) reveals a lattice spacing of 0.224 nm, which corresponds to the Pd (111) lattice plane. Further analyses using *ex-situ* EXAFS and *in-situ* FTIR, as shown in our recent study confirm the additional presence of single Pd atoms stabilized on the SnO₂ (110) surface[29]. The structural integrity of SnO₂ remained unchanged after Pd loading, and EDS mapping in Figure S4 confirms the uniform distribution of Pd, Sn, and O across the catalyst. X-ray photoelectron spectroscopy (XPS) was employed to further investigate the surface electronic state and composition of ADC Pd/SnO₂.

To further substantiate the successful coating of HMDS on the SnO₂ surface via the vapor-phase deposition method, XPS was conducted on both unmodified and HMDS-modified SnO₂ thin films, as illustrated in Fig. 3(a). The samples were prepared by depositing 30 nm SnO₂ thin films on silicon chiplets via atomic layer deposition (ALD), followed by the same HMDS modification process. The primary reason for utilizing ALD-deposited SnO₂ thin films, instead of drop-cast SnO₂ nanoparticle thin films used in the fabrication of gas sensors, is their high uniformity, which helps to avoid the influence of rough topography in XPS analysis. The XPS results indicate that the surface composition is substantially altered by the HMDS. The HMDS-modified SnO₂ exhibited a heightened C 1 s signal and a reduced O 1 s signal in comparison to the unmodified sample, which can be attributed to the carbon and oxygen content of HMDS and the chemical bonding of oxygen with SnO₂. Additionally, the unmodified sample showed more pronounced Sn signals, including Sn 3d_{3/2}, 3d_{5/2}, and 4d. This indicates that the HMDS coating effectively reduced the signal intensity of Sn signals, confirming successful surface modification. As shown in the high-resolution XPS scans in Fig. 3(b), the Pd 3d region exhibits two characteristic peaks at approximately 336 and 342 eV, each of which can be deconvoluted into two peaks. The spectra were fitted with four peaks, with the full width at half maximum (FWHM) of each kept the same for all peaks and the intensity ratio between 3d_{5/2} and 3d_{3/2} was maintained at 3:2. The peak positions and spin-orbit splitting align well with the literature. The prominent peak at 336 eV corresponds to Pd 3d_{5/2} at 337.4 eV and Pd-O bonding 3d_{5/2} at 336.1 eV, while the peak at 342 eV corresponds to Pd 3d_{3/2} at 342.8 eV

and Pd-O bonding 3d_{3/2} at 341.3 eV. This indicates that Pd exists not only in its atomic form on the SnO₂ support material but also in the form of PdO. Fig. 3(c) provides a detailed view of the O 1 s region from the spectra shown in Fig. 3(a), providing a comparative analysis of unmodified and HMDS-modified SnO₂ thin films. The HMDS-modified SnO₂ thin films display a broadened O 1 s region, which can be attributed to the formation of diverse oxygen-containing chemical bonds on the surface. These bonds result from the interaction between HMDS and the SnO₂ surface, leading to the development of a variety of oxide and siloxane bonds, including Si-O bonds in addition to Sn-O bonds. The Si-O bonds typically present with a binding energy of approximately 531.9 eV in the O 1 s region[36]. To further quantify the HMDS surface coverage, the HMDS film thickness was estimated using XPS intensity ratios, as detailed in Section S1 of the Supporting Information. This analysis is based on substrate signal attenuation and overlayer signal modeling. By applying well-established XPS equations to the experimental data, the HMDS film thickness was determined to be approximately 0.5 nm. As illustrated in Fig. 3(d), when HMDS adsorbs on the surface, its silicon-nitrogen (Si-N) bonds react with hydroxyl (-OH) groups on the surface, resulting in the formation of (trimethyl)silyl group (-Si(CH₃)₃) and release of NH₃ as a byproduct[21]. As the time progresses, additional HMDS molecules attach to the surface, ultimately forming a uniform organo-siloxane modified layer on the sample. This modification alters the chemical and physical properties of the surface, giving it hydrophobic properties (discussed next) that reduce interactions with water molecules or other polar molecules[37].

Following the confirmation of the successful HMDS coating on SnO₂, the macroscopic hydrophobicity changes induced by the HMDS modification on SnO₂ sensors were further investigated. Figs. 4(a) and 4(b) show the contact angle measurements of water droplets on unmodified and HMDS-modified SnO₂ thin films, respectively. Fig. 4(a) shows a contact angle of 12.3°, indicating the hydrophilic character of the unmodified SnO₂ surface. In contrast, Fig. 4(b) shows a significantly increased contact angle of 152.5° on the HMDS-modified SnO₂, highlighting the enhanced hydrophobicity. The observed increase in contact angle can be attributed to the formation of a methylated siloxane (-OSi(CH₃)₃) layer on the SnO₂ surface as a result of the HMDS modification.

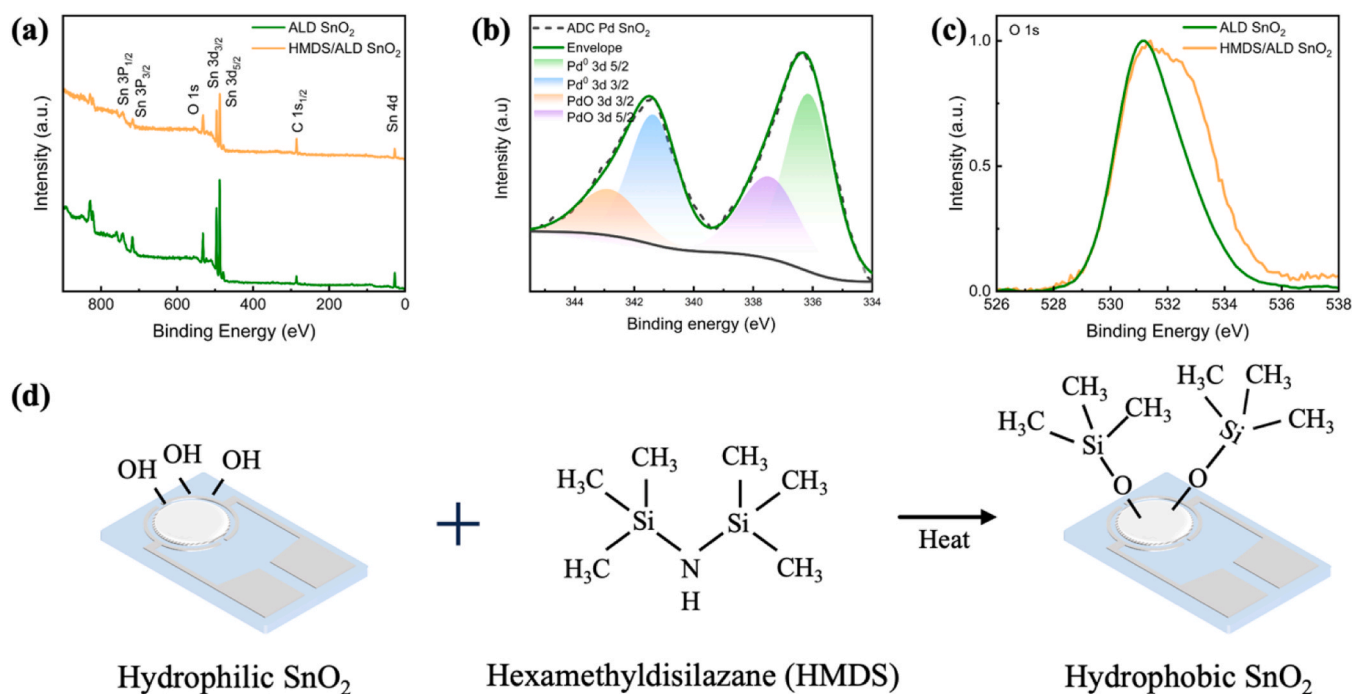


Fig. 3. (a) XPS of unmodified and HMDS-modified SnO₂ thin films. (b) High-resolution Pd 3d XPS region of the ADC Pd/SnO₂. (c) Detailed view of the O 1 s region from the spectra in (a). (d) Surface reaction scheme of the HMDS modification process for the ADC Pd/SnO₂ sensor.

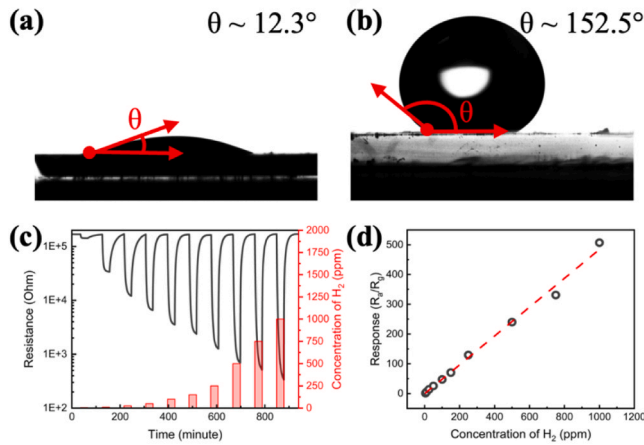


Fig. 4. Contact angle of water droplets on (a) unmodified ADC Pd/SnO₂ sensor and (b) HMDS-modified ADC Pd/SnO₂ sensor. (c) Real-time response and (d) parametric response of the HMDS-modified ADC Pd/SnO₂ sensor at 90°C to different hydrogen gas concentrations balanced with dry air.

The presence of methyl groups in this layer reduces the surface energy and affinity for water, leading to the observed increase in contact angle and hydrophobicity.

To determine whether surface hydrophobicity enhances humidity susceptibility of the sensor, the resistance of HMDS-modified SnO₂ sensors was measured at a range of relative humidities at an optimal operating temperature of 90°C, as shown in Figure S5(a). The influence of relative humidity on resistance variation was evaluated using the following definition of resistance change (%):

$$\Delta R(\%) = \frac{R_{dry} - R_{humid}}{R_{dry}} \times 100\% \quad (1)$$

where R_{humid} is the sensor resistance at a given humidity, and R_{dry} is the resistance measured under dry conditions. This formula allows for a clear comparison of the sensor's resistance shifts across different humidity levels, helping to evaluate the sensor's humidity susceptibility. As shown in Figure S5(b), the resistance changes across various SnO₂-based sensors, including unmodified SnO₂ sensors, ADC Pd/SnO₂ sensors, and HMDS-modified ADC Pd/SnO₂ sensors, was further analyzed under different humidity conditions at 90°C. It can be observed that all types of sensors exhibit a decrease in resistance as the relative humidity increases. In dry conditions, SnO₂ gas sensors adsorb oxygen (O₂), leading to the dissociative adsorption of oxygen (O) and the subsequent trapping of electrons from SnO₂, as expressed by the following reactions [38]:



As relative humidity rises, water vapor in the atmosphere blocks the adsorption of oxygen on the surface, a phenomenon known as hydroxyl poisoning[39]. The reaction of surface-adsorbed oxygen with water vapor leads to the transfer of trapped electrons back to SnO₂, as expressed by the following reaction[38,40]:



The most notable change in resistance occurs when relative humidity rises from a dry environment to a level of 16 %. Although resistance continues to vary with increasing relative humidity, the overall trend tends to saturate compared to the sharp variation observed during the initial shift. In addition, the enhancement in humidity susceptibility observed in SnO₂ sensors after loading ADC Pd can be attributed to the modification of the surface chemistry of SnO₂ by the presence of Pd. The

adsorbed oxygen species on Pd are stabilized, particularly in humid conditions, thereby preventing their replacement by OH⁻ ions[41]. Following the HMDS modification of ADC Pd SnO₂ sensors, the majority of previously adsorbed OH⁻ ions on the SnO₂ surface are replaced by a layer of methylated siloxane. This replacement reduces the number of hydroxyl groups available to interact with water molecules, thereby decreasing resistance change and further enhancing the sensor's humidity susceptibility.

3.2. Gas sensing performance

When evaluating the response of the sample to hydrogen gas, a relatively low concentration of 50 ppm prevents the sensor from being exposed to high gas levels at an early stage, which could lead to irreversible changes in the material and damage to the sensor. This concentration facilitates the assessment of the sensor's linear range and fundamental material properties. Furthermore, since the permissible concentration of hydrogen in industrial environments is typically governed by safety regulations, this approach aligns with practical safety considerations. Figure S6(a) shows the real-time response of the HMDS-modified ADC Pd/SnO₂ sensor to 50 ppm hydrogen at 90°C. It also illustrates the definitions for response, and response and recovery times. Upon the introduction of hydrogen, the sensor resistance decreases, which is consistent with the typical behavior of n-type metal oxide semiconductors when exposed to reducing gases. The sensor response is determined using the following equation[42]:

$$Response = \frac{R_a}{R_g} \quad (5)$$

where R_a represents the resistance of the sensor in air and R_g denotes the resistance of the sensor in the presence of the gas. To gain further insight into the sensor's performance, both response time and recovery time are measured. Response time is defined as the duration required for the sensor to detect a target gas and achieve a 90 % change in resistance from its initial value. In contrast, recovery time is the period it takes for the sensor's resistance to return to 90 % of its initial value after the target gas has been removed and returned to its initial concentration. The hydrogen sensing performance of the HMDS-modified ADC Pd/SnO₂ sensor was evaluated across different operating temperatures to find the optimum. Figure S6(b) depicts the sensor's response to 50 ppm hydrogen under a range of operating conditions. The maximum response is found at 90°C, with lower values at 60°C and 120°C. The alteration in sensor resistance upon exposure to hydrogen is attributed to the redox reaction between hydrogen molecules and chemisorbed oxygen species on the surface of the sensing materials[14]. At relatively low operating temperatures, this reaction lacks sufficient energy, which results in low sensitivity and long response time. Conversely, at relatively high temperatures, gas molecules may desorb from the surface of the sensing materials before the reaction can occur, which again reduces the sensor response. Accordingly, the majority of researchers propose an optimized operating temperature for SnO₂ gas sensors[43], which is determined by the competition between temperature-dependent physical adsorption and chemical adsorption on the material's surface[44]. Taking into account the response, response/recovery times, and the potential decomposition of HMDS at temperatures exceeding its boiling point of 125°C, operating temperature of 90°C was identified as optimal for hydrogen sensing in this present study.

Furthermore, the long-term stability of the sensor is crucial in the context of practical applications. To assess the stability of HMDS at 90°C over time, a long-term stability test was conducted, as shown in Figure S7. The contact angle of the HMDS film on a silicon chip was measured under continuous heating at 90°C for 1000 h. The results demonstrated that the HMDS film remained stable over a long period of time.

Fig. 4(c) shows the real-time response curves of the sensor at its

optimal operating temperature of 90°C with hydrogen concentrations ranging from 10 to 1000 ppm, balanced in air. Upon exposure to hydrogen, the sensor resistance rapidly decreases before stabilizing. After the target gas is removed, the sensor resistance reverts to its baseline and stabilizes again. The ability of the sensor to return to its baseline indicates its reversibility and stability. The sensor's strong capability for quantitative hydrogen detection is attributed to the reversible adsorption and desorption of hydrogen molecules on the sensor surface, ensuring reliable and accurate detection. To further investigate the relationship between concentration and response, concentration–response curves were calculated and fitted. Fig. 4(d) depicts the sensor's response to hydrogen concentrations from 10 to 1000 ppm at 90°C. The data demonstrate a notable linear relationship across the entire concentration range investigated, confirming the sensor's efficacy for hydrogen detection. The sensor exhibits satisfactory resolution for low gas concentrations, accurately detecting hydrogen at levels as low as 10 ppm, with an effective response of 4.9 at 90°C. This performance meets the requisite standards for reliable hydrogen detection across low to moderate gas concentrations, ranging from 0.01 % to 10 % [45]. The repeatability of the HMDS-modified SnO₂ sensor was evaluated to ascertain its practical applicability.

The incorporation of palladium into the sensor design markedly enhances the sensor's sensitivity, attributable to palladium's efficient catalytic capability. This improvement results from the effective dissociation of both oxygen and hydrogen molecular adsorbates on Pd surfaces, followed by the diffusion of the resulting atomic species and their subsequent chemisorption onto the SnO₂ surface, which further amplifies the overall sensitivity of the sensor [46]. In addition, in comparison to other noble metals, Pd exhibits a particular solubility for hydrogen at room temperature. This property enables palladium to interact effectively with hydrogen molecules in a manner that optimizes its performance as a hydrogen sensor [47]. However, under suitable temperatures and pressures, hydrogen's high solubility can lead to diffuse into the palladium bulk, forming a minor quantity of palladium hydride (PdH_x). This phenomenon may contribute to slower recovery times and hysteresis [48–50]. During this process, hydrogen molecules are incorporated into the palladium lattice, forming bonds with palladium atoms. The formation of palladium hydride can alter the palladium lattice by replacing or filling vacancies with hydrogen atoms, thereby

modifying the electronic structure and physical properties of palladium. Such changes may impact the efficacy of the catalyst and the dynamics of hydrogen adsorption and desorption, resulting in fluctuations in sensor performance [49].

For a gas sensor to function effectively and reliably, it is essential that the response to a specific concentration of hydrogen remain consistent. This should be achieved with minimal or no interference from other substances or fluctuations in the ambient environment. Moisture, in particular, significantly affects the performance and accuracy of gas sensors, particularly those based on metal oxide semiconductors. The interaction between water molecules and target gas molecules on the sensor surface can result in competition for active sites, which may influence the adsorption and reaction processes. This competition may result in variations in sensor response and overall effectiveness. Even at relatively low relative humidity, the majority of SMOx sensors are significantly impacted [51]. As humidity rises, the adsorption of water molecules can hinder the adsorption of gas molecules, reducing the sensitivity of the sensor [14]. Fig. 5(a) presents the real-time response of both the unmodified ADC Pd/SnO₂ sensor and the HMDS-modified ADC Pd/SnO₂ sensor to 50 ppm hydrogen gas in dry air and at relative humidity levels of 25 %, 50 %, and 75 %, all measured at a working temperature of 90°C. Additionally, Figure S8 presents the real-time response of the unmodified ADC Pd/SnO₂ sensor and the SnO₂ sensor (i.e., without Pd) to 50 ppm hydrogen in dry air at 90 °C for comparison, highlighting the enhanced sensor response of ADC Pd/SnO₂ sensor.

Fig. 5(b) shows the further calculated response results of both sensors under varying relative humidity. As the relative humidity increased, the response of both sensors to hydrogen gas decline. This reduction is expected, as adsorbed water molecules limit the availability of active sites for hydrogen, leading to a competing surface reaction that diminishes the sensor's response. Although the response of the HMDS-modified sensor decreases with rising relative humidity, the decline is much less pronounced than for the unmodified sensor. It can thus be concluded that the HMDS modification effectively mitigates the impact of humidity on sensor performance. Figs. 5(c) and 5(d) show the calculated response time and recovery time for both sensors, respectively, under varying relative humidity. The response time is shorter than the recovery time, suggesting that the adsorption and reduction of hydrogen on the material's surface occur more rapidly than the subsequent desorption and

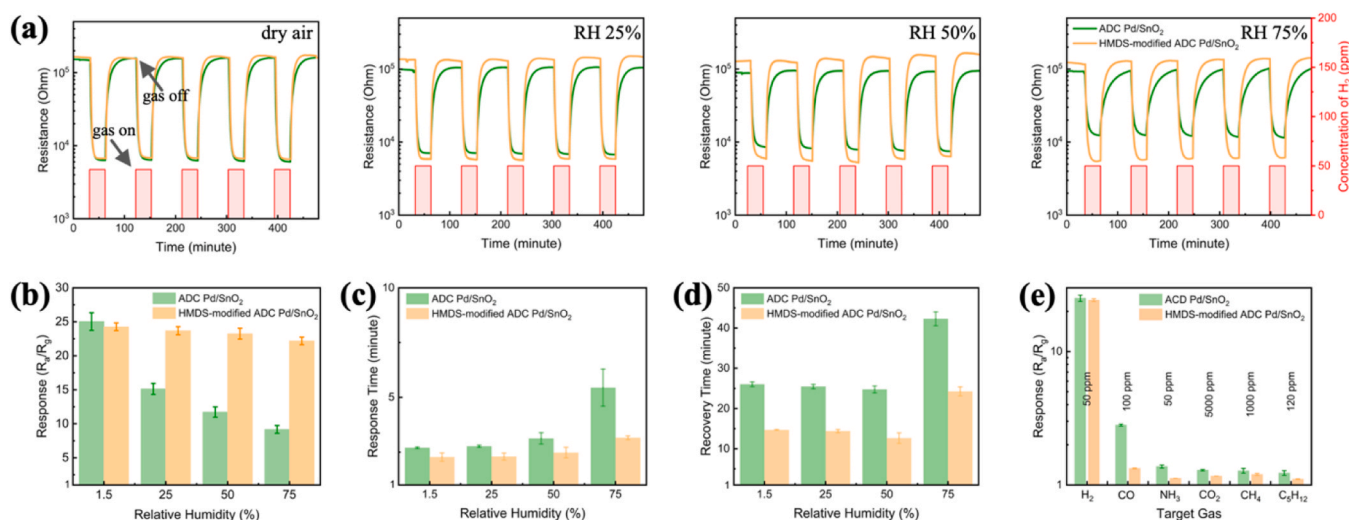


Fig. 5. (a) Real-time response of the unmodified ADC Pd/SnO₂ sensor and the HMDS-modified ADC Pd/SnO₂ sensor to 50 ppm hydrogen gas under varying relative humidity levels, including dry air (equivalent to 1.5 % relative humidity), 25, 50, and 75 %. The relative humidity was set at 25°C before the gas entered the test chamber. During measurements, the sensor heater was maintained at 90°C, while the total pressure inside the chamber remained at atmospheric pressure. Bar charts (b) through (d) summarize the data from (a), showing (b) sensor response, (c) response time, and (d) recovery time for both sensors under the same relative humidity and temperature. (e) Bar charts comparing the selectivity of both sensors at 90°C in dry air, depicting their responses to various gases at different concentrations, with all gases balanced in dry air.

oxidation processes[52]. Both sensors exhibit an increasing trend in response and recovery times as relative humidity rises. The electrical response of the sensing material to humidity is related to both the chemical and physical adsorption of water, which competes with hydrogen molecules for active sites. At low relative humidity, water molecules primarily undergo chemisorption via dissociation mechanisms, forming two hydroxyl ions per water molecule at the available active sites on the SnO₂ surface. As humidity increases, additional water molecules are physisorbed, forming double hydrogen bonds with hydroxyl groups from the previous water layer. This process contributes to the longer response and delayed recovery times observed at higher humidity levels[53,54]. However, the HMDS-modified ADC Pd/SnO₂ sensor consistently shows shorter response and recovery times than the unmodified sensor across all relative humidity levels. Specifically, at 75 % relative humidity, the sensor's response time decreased from 5.4 to 3.1 min after HMDS modification, while the recovery time dropped from 42 to 24 min. This indicates that the HMDS treatment effectively reduces the formation of hydroxyl groups by chemisorption and limits the successive physical adsorption of water molecules that accumulate on the surface with increasing humidity.

Selectivity is a crucial factor for gas sensors. A reduced probability of the sensor misidentifying non-target gases as the target gas increases the reliability and accuracy of measurements[55]. The responses of the unmodified and HMDS-modified ADC Pd/SnO₂ sensors at 90 °C to H₂, CO, CH₂O, NH₃, CO₂, CH₄, and C₆H₁₂ are demonstrated in Fig. 5(e). The concentrations of these gases were referenced from the Permissible Exposure Limits established by the U.S. Department of Labor's Occupational Safety and Health Administration. An inspection of the unmodified sensor shows a response of 25.0 for H₂ and 4.0 for CO, while the responses to other gases are all less than 1.4. This indicates an inherent selectivity in the Pd-loaded SnO₂ sensor. Real-time response of the unmodified ADC Pd/SnO₂ sensor and the HMDS-modified ADC Pd/SnO₂ sensor to CO, NH₃, CO₂, CH₄, and C₆H₁₂, as shown in Figure S9–S13. The observed selectivity is particularly noteworthy in light of the role of Pd in the enhancement of sensor performance. The incorporation of palladium into the sensor material has been demonstrated to markedly enhance the selectivity of SnO₂ gas sensors. Palladium, known for its superior catalytic properties, facilitates the dissociation of gas molecules on its surface, particularly hydrogen, while its catalytic activity towards other gases is comparatively weaker[56, 57]. This results in enhanced sensitivity to hydrogen, thereby improving its selectivity. In comparison to the unmodified sensor, the HMDS-modified ADC Pd/SnO₂ sensor exhibits a slight reduction in response to hydrogen under identical conditions. Nevertheless, a notable reduction in reactivity towards other gases was also observed. These results suggest that while the HMDS modification minimally affects hydrogen interactions, it effectively reduces interference from other gases.

To further evaluate the response repeatability of the HMDS-modified ADC Pd/SnO₂ sensor under both dry and humid conditions, long-term

cycling tests were conducted. Fig. 6(a) illustrates the sensor's response when exposed to 50 ppm hydrogen across 54 testing cycles over a duration exceeding 72 h at 90 °C under dry conditions. The sensor exhibited a stable response an average response of 24.1 ± 1.3 . No significant variation was observed throughout the test, and the sensor consistently returned to its baseline after each cycle, indicating excellent recovery and reusability. Fig. 6(b) presents the repeatability test conducted under 75 % relative humidity. Over 33 cycles conducted across more than 48 h, the sensor maintained a stable average response of approximately 21 ± 1.1 , without notable degradation. This result further confirms that HMDS surface modification ensures stable and reliable sensor performance even in humid environments.

3.3. Proposed gas sensing mechanism for HMDS-modified ADC Pd/SnO₂

To further illustrate the impact of surface modifications on sensor performance under diverse conditions, Fig. 7 depicts the schematic representation of the gas sensing model for HMDS-modified ADC Pd/SnO₂. The HMDS treatment reduces the response to all gases, which indicates that the intrinsic properties of the HMDS layer affect the diffusion and reaction processes of the gases. Upon reacting with the material surface, HMDS forms a thin organic silane film comprising two silicon atoms and six methyl (–CH₃) substituents. The formation of this thin film significantly reduces the number of polar functional groups on the material surface, leading to a decrease in surface energy. This reduction makes it more difficult for polar molecules to adhere, resulting in a markedly diminished response to polar gases, such as carbon monoxide, formaldehyde, and ammonia, with the most pronounced decrease observed for carbon monoxide. Additionally, the HMDS layer impacts the diffusion of all gas molecules to the SnO₂ surface. Due to its small size and high diffusion capability, hydrogen can effectively penetrate the HMDS layer and react on the catalyst surface more

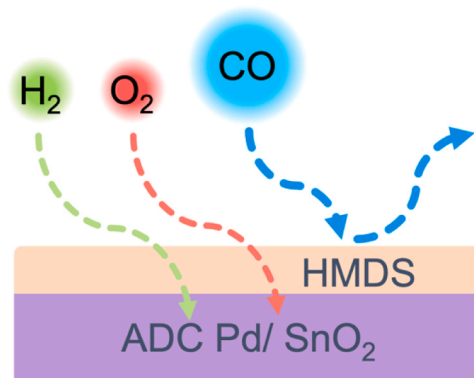


Fig. 7. Schematic drawing of gas sensing model for HMDS-modified ADC Pd/SnO₂ sensor.

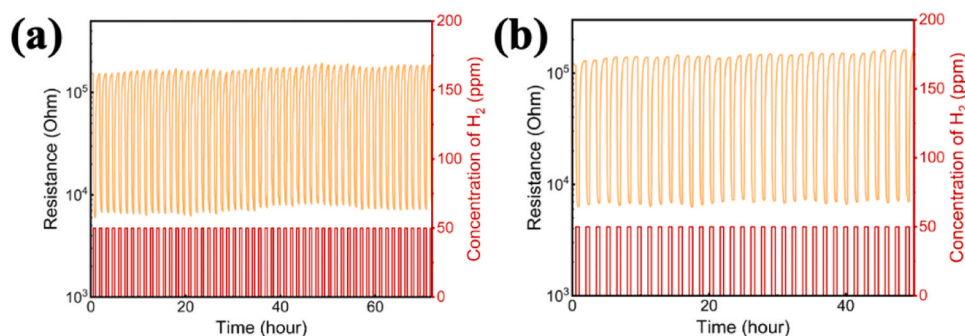


Fig. 6. Repeatability tests of the HMDS-modified ADC Pd/SnO₂ sensor exposed to 50 ppm hydrogen at 90 °C under (a) dry conditions and (b) 75 % relative humidity, demonstrating stable and consistent response values over 54 and 33 testing cycles, respectively, spanning more than 72 and 48 h.

efficiently than larger molecules. Furthermore, hydrogen's non-polar nature minimizes the hindrance from the HMDS layer. In addition, due to the Pd loading, Pd is present in both its metallic form Pd and as PdO, and is finely dispersed on the SnO₂ surface. Metallic Pd very efficiently adsorbs and catalyzes of both oxygen and hydrogen molecules, facilitating the diffusion of the resulting atomic species and their subsequent chemisorption onto the SnO₂ surface[36]. In contrast, the oxidized form of palladium, PdO, promotes the oxidation of hydrogen through the surface oxygen anions (O⁻), ultimately leading to the formation of water. This synergistic effect of Pd and PdO on the SnO₂ surface enhances the efficiency of hydrogen catalysis. Overall, the presence of a dense and thin HMDS layer, combined with the characteristics of the ADC Pd-SnO₂ materials, effectively minimizes the diffusion of gases other than hydrogen through the HMDS to the SnO₂ surface. This reduction in gas diffusion significantly contributes to the sensor's enhanced selectivity, particularly for hydrogen.

4. Conclusion

In conclusion, a chemiresistive gas sensor with a superhydrophobic sensing layer of ADC Pd/SnO₂, demonstrating advanced hydrogen detection capabilities, has been successfully developed. Pd loading significantly enhances the sensor's sensitivity to hydrogen by facilitating the adsorption and catalytic conversion of hydrogen molecules, even at relatively low temperatures. Furthermore, the application of a methylated siloxane layer through the HMDS modification reduces surface energy and water affinity, which enhances the sensor's resistance to moisture and minimizes variations in sensor resistance under different humidity conditions. Additionally, the HMDS layer reduces the presence of polar functional groups, thereby limiting the adhesion of polar gases such as carbon monoxide, formaldehyde, and ammonia. Moreover, the thin, dense HMDS layer restricts the diffusion of larger gas molecules but allows smaller ones like hydrogen to penetrate, thereby enhancing the sensor's selectivity. The combination of HMDS surface modification and the intrinsic properties of the ADC Pd/SnO₂ material enables the sensor to maintain a notable response to hydrogen at low temperatures while maintaining superior detection capabilities in high-humidity environments.

CRedit authorship contribution statement

Ilya Gurin: Writing – review & editing, Resources. **Haimei Zheng:** Formal analysis. **Nishit Goel:** Writing – review & editing, Resources. **Hyo Jun Min:** Methodology. **Yi Chen:** Formal analysis. **Wei Tzu Chiao:** Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, Conceptualization. **Yaprak Ozbakir:** Writing – review & editing, Methodology. **Roya Maboudian:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Stephen Bart:** Writing – review & editing, Resources. **Carlo Carraro:** Writing – review & editing, Resources, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was supported by the U.S. National Science Foundation under grant no 2224465, and the industrial members of the Berkeley Sensor & Actuator. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U. S. Department of Energy under contract no DE-AC02-05CH11231.Y.C. and H.Z. also acknowledge the support of the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (BES), Materials Sciences and

Engineering Division under Contract No. DE-AC02-05-CH11231 within the in-situ TEM program (KC22ZH). The authors would like to express their sincere gratitude to the Materials Sciences Division at Lawrence Berkeley National Laboratory, and especially to Dr. Diyi Cheng, for his expert assistance in acquiring the high-resolution FESEM images used in this study.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.snb.2025.138335](https://doi.org/10.1016/j.snb.2025.138335).

Data availability

No data was used for the research described in the article.

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