Highly Sensitive and Selective Detection of Hydrogen Using Pd-Coated SnO$_2$ Nanorod Arrays for Breath-Analyzer Applications

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Abstract: We report a breath hydrogen analyzer based on Pd-coated SnO$_2$ nanorods (Pd-SnO$_2$ NRs) sensor integrated into a miniaturized gas chromatography (GC) column. The device can measure a wide range of hydrogen (1–100 ppm), within 100 s, using a small volume of human breath (1 mL) without pre-concentration. Especially, the mini-GC integrated with Pd-SnO$_2$ NRs can detect 1 ppm of H$_2$, as a lower detection limit, at a low operating temperature of 152 °C. Furthermore, when the breath hydrogen analyzer was exposed to a mixture of interfering gases, such as carbon dioxide, nitrogen, methane, and acetone, it was found to be capable of selectively detecting only H$_2$. We found that the Pd-SnO$_2$ NRs were superior to other semiconducting metal oxides that lack selectivity in H$_2$ detection. Our study reveals that the Pd-SnO$_2$ NRs integrated into the mini-GC device can be utilized in breath hydrogen analyzers to rapidly and accurately detect hydrogen due to its high selectivity and sensitivity.

Keywords: breath hydrogen analyzer; gas sensor; Pd-coated SnO$_2$ nanorods; gas chromatography; selectivity

1. Introduction

Humans are hosts to over 1000 species of microbes [1] that are responsible for human health and disease [2]. Important and promising studies have identified the effects of the human microbiome on disease conditions, such as obesity [3,4], diabetes [5,6], irritable bowel syndrome [7,8], fatty liver [9], and many others [10,11]. The majority of the microbes in the body inhabit the gastrointestinal tract, giving a chance for these organisms to influence metabolism, immunity, and digestion [12]. It is known that the gastrointestinal tract produces various gases, such as hydrogen, carbon dioxide, methane, and hydrogen sulfide, as the products of intestinal microbial metabolism, colonization, and subsequent fermentation [12]. Most of the gases are absorbed through the lining of the large intestine into the bloodstream. Then, the gases are transported to the lungs via the bloodstream where they are exchanged into the airways of the lungs and exhaled [13].

The source of H$_2$ in the breath can be from the bacterial fermentation of carbohydrates in the bowel caused by gastrointestinal diseases. Patients with gastrointestinal disorders have more aggressive fermentation, which results in premature and excessive amounts of H$_2$ due to inordinate microbial colonization [14]. The phenomenon is known as small intestinal bacterial overgrowth (SIBO). Therefore, some symptoms of irritable bowel syndrome (IBS) can be described by SIBO, and it can be diagnosed by the hydrogen breath test. However, the hydrogen breath test with lactulose can only diagnose one-third of the patients with SIBO, and the glucose hydrogen breath test is well-known to be highly specific for SIBO diagnoses [14]. On the other hand, some patients with IBS produce gases, such
as methane and hydrogen sulfide with or without hydrogen. In particular, patients with constipation may have higher methane contents, whereas patients with diarrhea, such as those with ulcerative colitis and Crohn’s disease, may have higher hydrogen content [14,15]. Thus, hydrogen and methane have the potential for use as biomarkers for diarrhea and constipation, respectively. Accordingly, hydrogen breath tests can be useful for diagnosing many gastroenterological disorders, such as lactose and fructose malabsorption [16], celiac disease [10], Crohn’s disease, and ulcerative colitis [15].

Relatively accurate hydrogen concentration measurements in the breath can be realized using various instrumentation. Nielsen et al. first introduced chromatographic techniques for quantitatively measuring small amounts of H$_2$ and CH$_4$ in breath samples and applied this method to humans [17,18]. Based on Nielsen’s approach, various detectors, such as gas chromatography (GC) integrated with solid-state sensors [15,19,20], an infrared sensor combined with an electrochemical sensor [21], and a pulsed-discharge helium ionization detector (PHID) coupled with GC [22,23], have been developed to measure H$_2$ and CH$_4$ in breath samples. Among them, Raman gas spectroscopy exhibits excellent chemical selectivity for various gases in complex mixtures [24,25]. However, most instruments for measuring breath hydrogen and methane are still expensive, not portable, and complex. It is, therefore, necessary to develop such instruments with inexpensive and miniaturized components and simplified detection procedures.

To develop a compact analyzer, it is critical to find high-performance sensing materials. Metal-oxide-semiconductor (MOS) based sensors can be used in a portable gas sensing system owing to several of their advantages, including high-sensitivity, fast response-time, compact size, and low cost. Specifically, it is easy to fabricate nanostructures to achieve high-sensitivity [26–31]. Many metal oxides, including SnO$_2$, ZnO, WO$_3$, TiO$_2$, In$_2$O$_3$, Nb$_2$O$_5$, FeO, NiO, Fe$_2$O$_3$, Ga$_2$O$_3$, MoO$_3$, Sb$_2$O$_3$, and V$_2$O$_5$, which exhibit a large variation in electrical resistance after exposure to hydrogen gas, have been investigated for use as hydrogen sensing materials in MOS [27,28]. Among the MOS sensing materials, SnO$_2$ has been widely used to detect H$_2$ because of its high-sensitivity [29]. Additionally, the hydrogen sensing performance of SnO$_2$ has been further enhanced by utilizing noble metals [30]. Notably, Pd is the most widely used metal for enhancing the sensing response of H$_2$ and decreasing the optimal working temperature [29,31]. However, most studies conducted on SnO$_2$-based hydrogen sensors have focused on detecting H$_2$ leakage during storage/transport/use and detecting H$_2$ dissolved in transformer oil; it has been found that the lowest detection limit is 4% for the former [32] and 100–500 ppm for the latter [33]. Both results are much higher than that of the concentration of breath hydrogen. The concentration of breath hydrogen is approximately 2 ppm [34] in healthy people and greater than 10 ppm [35] in patients with carbohydrate malabsorption. Therefore, research concerning SnO$_2$-based hydrogen sensors for the application of the exhaled breath analyzer is valuable. Furthermore, selective detection of target gas in a mixed gas is a significant obstacle in MOS sensors such as those based on SnO$_2$. Consequently, it is necessary to adopt GC to resolve the selectivity issue of MOS sensors.

In this work, we investigated the sensing performance of Pd-coated SnO$_2$ nanorod arrays (NRs) integrated with a miniaturized GC column to detect H$_2$ selectively for an application of a breath hydrogen analyzer. The H$_2$ sensing properties of the breath analyzer were investigated based on the sensing responses at various concentrations of H$_2$ (1–100 ppm). The selectivity of the breath analyzer for detecting H$_2$ was studied by exposing it to mixtures of gases, such as H$_2$, CO$_2$, N$_2$, CH$_4$, and CH$_3$COCH$_3$. We compared the Pd-SnO$_2$ NRs with ZnO nanoparticles, which lack selectivity in detecting H$_2$. We also discuss the humidity effect on the sensing performance of the breath hydrogen analyzer.

2. Materials and Methods

2.1. Fabrication and Characterization

The vertically oriented SnO$_2$ nanorods (NRs) were synthesized on an Al$_2$O$_3$ substrate (5 × 2.5 mm$^2$) by the glancing angle deposition method (GLAD) using an electron-beam
evaporator. In the GLAD method, by adjusting the incident angle of the vapor flux and the substrate rotation speed, vertically ordered nanorod arrays with high-density, as well as nanorods of uniform diameter and length can be fabricated [31]. Before the synthesis of the NRs, a DC sputtering system was used to fabricate interdigitated electrodes (Pt, 100 nm in thickness) and a heater (Pt, 600 nm in thickness) on the top and bottom of the alumina substrate, respectively. The patterned alumina substrate was loaded onto the sample holder in the sputtering system. SnO$_2$ granules (99.99% Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) that had an average size of 3 mm were placed in a crucible that was located 50 cm below the sample holder. The sample holder was tilted at 80$^\circ$ and rotated at a speed of 15 rpm during the growth of the SnO$_2$ NRs. Electron-beam evaporation was performed with a 1 Å/s deposition rate at a base pressure of $5.0 \times 10^{-6}$ Torr. The as-deposited sample was annealed at 550 $^\circ$C for 2 h. After the synthesis of the SnO$_2$ NRs, a 5 nm Pd layer was deposited on the annealed SnO$_2$ NRs with a power of 20 W in an Ar atmosphere using an ultra-high vacuum DC magnetron sputtering system. The base pressure was 4.1 $\times 10^{-8}$ Torr, and the deposition process was conducted at a pressure of less than 2.3 $\times 10^{-3}$ Torr with an Ar flow rate of 34 SCCM. A high-purity Pd target (4N) was used, and the Pd deposition rate was ~4.7 Å/s at room-temperature. The morphology and the compositional analysis of the Pd-SnO$_2$ NRs were examined by a field emission scanning electron microscope (FE-SEM, JSM-7001F, JEOL Ltd., Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (FE-SEM-EDX, JSM-7001F, JEOL Ltd., Tokyo, Japan).

ZnO NPs also were prepared by using a wet chemical method in order to compare the sensing performance of the Pd-SnO$_2$ NRs to the ZnO nanoparticles (NPs) recently developed by our group [36]. The synthesized ZnO NPs were dispersed in methanol. More details of the synthesis method for ZnO NPs are available in our previous work [36]. The sensor was fabricated by dropping the ZnO NPs solution onto the patterned Al$_2$O$_3$ substrate and heat-treated at 600 $^\circ$C for 30 min.

2.2. Gas Sensing Test

We conducted an H$_2$ sensing test using miniaturized gas chromatography (mini-GC). Figure 1 shows the mini-GC that had the dimensions of 8 cm $\times$ 13 cm $\times$ 16 cm. The mini-GC gas analyzer consisted of a sensor based on Pd-SnO$_2$ NRs, a packed column, a sampling loop (1 mL), a mini-sized pump, and three solenoid valves. The sampling volumes of the gases were limited to 1 mL. We use dry air as a carrier gas to continuously supply oxygen ions to the surface of the Pd-SnO$_2$ NRs because the gas sensing mechanism of metal-oxide semiconducting materials, such as SnO$_2$, is based on changes in the thickness of the depletion layer by oxygen ion adsorption onto the surface. The flow rate of the carrier gas affects the sensing response because the sensing material requires a certain amount of time to react with the gas. Herein, the flow rate of the carrier gas was adjusted using a flow control valve and maintained 30 SCCM for analysis. Prior to injection into the GC system, the ambient air was passed through a filter filled with silica gel to remove any moisture.

We chose a packed GC column because of its huge surface area, low cost, and good operability at room-temperature [37]. The packed column was filled with a packing material coated with the stationary phase (Isonlab Inc., Seongnam-si, South Korea) and the column’s inner diameter was 0.15 cm. The length of the column was adjusted to 30 cm to achieve a short retention time of the target gas. Gas separation occurs during the mixture of gas passing through the column, due to the differing interaction strengths between the various gas molecules and the stationary phase. The interaction strength is related to the polarity and size of the gas molecules and the stationary phase of the packed column was weakly polar. Thus, small non-polar gases, such as H$_2$, N$_2$, and CO$_2$, were quickly released from the column owing to their weak interactions while larger polar gases, such as acetone, were slowly released owing to their strong interactions with the stationary phase.
Figure 1. Schematic illustration of a hydrogen analyzer using a miniaturized gas chromatography (mini-GC).

The sensing process of the breath hydrogen analyzer based on Pd-SnO$_2$ NRs is described as follows. First, a 1 mL mixture of the target gas and ambient air was used to fill the sampling loop for 100 s without pre-concentration. Subsequently, the sampled gas was injected into the packed column and the components of the gas were separated by the interaction between the stationary phase and gas molecules as they passed through in the packed column. The temperature of the column was maintained at room-temperature (30 °C) by controlling the thermostat. The target gas that passed through the column was detected by the Pd-SnO$_2$ NR or ZnO NPs. To optimize the working temperature of the sensor, the sensor response was tested at various temperatures, i.e., 25, 80, 115, 139, 152, 165, 178, and 191 °C. The ability of the analyzer to sense the presence of H$_2$ was checked at various concentrations of H$_2$ in the range of 1–100 ppm at the optimal working temperature. The hydrogen concentration was controlled by changing the mixing ratio between highly concentrated hydrogen in an airbase and synthetic air using a mass flow controller. The selectivity of the mini-GC system for H$_2$ was investigated by measuring its responses when exposed to various gases, including H$_2$, CO$_2$, N$_2$, CH$_4$, and CH$_3$COCH$_3$ and comparing its responses to those of ZnO nanoparticles.

The sensing performance was evaluated based on the resistance of the sensor, and the resistance obtained in the gas analyzer was converted to a sensor signal (log(R)). The change in the sensing signal of the samples was defined as $\Delta \log(R)$ [38].

$$\Delta \log(R) = \log(R)_{\text{max}} - \log(R)_{\text{min}},$$  

where $\log(R)_{\text{max}}$ and $\log(R)_{\text{min}}$ are the maximum and minimum values before and after exposure to H$_2$, respectively.
2.3. Gas Sensing Mechanism

Figure 2 shows the underlying sensing mechanism of the Pd-SnO2 NRs for the detection of H2. When the Pd-SnO2 NRs were exposed to air, oxygen molecules in the air were adsorbed on the surfaces of the Pd nanoparticles (NPs) and the SnO2 NR. The adsorbed oxygen molecules took the electrons from the conduction band of the SnO2 NR and formed anionic oxygen species (O\textsuperscript{2−}, O\textsuperscript{−}, and O\textsuperscript{−}) depending on the working temperature. At temperatures greater than 150 °C, O\textsuperscript{−} and O\textsuperscript{2−} were chemisorbed \([39,40]\). O\textsuperscript{−} commonly is chemisorbed at low temperatures \((T < 150 °C)\) \([41]\). Since the working temperature of SnO2 NR was in the range of >150 °C, the O\textsuperscript{−}, and O\textsuperscript{2−} ions were adsorbed on the surface of the SnO2 NRs. In addition, oxygen molecules can be adsorbed on the surface of the Pd NPs and be easily dissociated into O\textsuperscript{−} ions due to the spillover effect of the Pd metal \([42]\). Due to the higher work function of Pd metal \((\Phi_{Pd} = 5.12 \text{ eV})\) compared to that of SnO2 \((\Phi_{SnO2} = 4.9 \text{ eV})\), a Schottky barrier was formed at the interface between Pd and SnO2 \([43]\), and the electrons that were associated with SnO2 were transferred to the Pd metal. This resulted in the enhanced dissociation of oxygen molecules into O\textsuperscript{−} ions on the surface of the Pd NPs, and these ions easily diffused into the surface vacancies of the SnO2 NR. Consequently, thicker electron depletion layers were formed at the interface between the Pd NPs and the SnO2 NR. This infers that a greater number of reactive sites for H2 was produced on the surface of the Pd-SnO2 NR.

\[
\text{H}_2\text{(gas)} \rightarrow 2\text{H}\text{(adsorb)} \tag{2}
\]

\[
2\text{H}\text{(adsorb)} + \text{O}^-\text{(adsorb)} \rightarrow \text{H}_2\text{O} + \text{e}^- \tag{3}
\]

Figure 2. Schematic image of the sensing reaction mechanism of Pd-coated SnO2 NR arrays in air and hydrogen.

When the Pd-coated SnO2 NRs were exposed to H2, the H2 molecules decomposed into hydrogen atoms (Equation (2)). The dissociated hydrogen atoms change Pd into PdHx \([44]\), leading to a reduction in the work function of Pd \((\Phi_{Pd} > \Phi_{PdHx})\) and a decrease in the height of the Schottky barrier. In addition, the hydrogen atoms reacted with a large number of the O\textsuperscript{−} ions (Equation (3)) that were formed at the initial state of the surface of the sample. According to the reaction in Equation (3), electrons are returned to the conduction band of SnO2. Therefore, the thickness of the depletion layer is reduced, thereby decreasing the resistance of the Pd-SnO2 NR.

3. Results and Discussion

Figure 3 shows an image of the as-synthesized Pd-SnO2 NR. Figure 3a,b show the top and cross-sectional views, respectively, of the SEM images of the Pd-SnO2 NRs grown on the Al2O3 substrate. Figure 3a is a magnified view of Figure 3a. The SEM image (top-view) shows that the SnO2 NRs predominantly were clustered and located randomly. The diameters of the NR clusters were 40–200 nm, and the distances between the adjacent clustered NR ranged from 5 to 40 nm. Figure 3c shows that the clusters consisted of small
grains (~40 nm). This indicated that the diameter of the SnO$_2$ NR was about 40 nm. The cross-sectional-view SEM image of Figure 3b shows that all of the SnO$_2$ NRs were aligned vertically with respect to the substrate, and the average height of the SnO$_2$ NR was 250 nm. Figure 3d shows the EDX mapping images of the cross-sectional-view SEM image, and it shows the SnO$_2$ NR on the Al$_2$O$_3$ substrate. The deposited Pd nanoparticles were dispersed uniformly on the top and side surfaces of the SnO$_2$ NRs.

The sensing properties of Pd-SnO$_2$ NRs in the mini-GC system were tested for various H$_2$ contents. Figure 4a shows the H$_2$ sensing response of the Pd-SnO$_2$ NRs integrated with mini-GC to 100 ppm of H$_2$ as a function of operating temperature. The optimal working temperature of the sensor was 152 °C. The response increased and reached a maximum at 152 °C, after which it decreased with increasing temperature. These results were due to the competition between the slow kinetics at lower temperatures and improved desorption at higher temperatures.

Figure 4b shows the variation with time of the sensor signal (log($R$)) of the Pd-SnO$_2$ NRs integrated with mini-GC for various H$_2$ concentrations (1–100 ppm) at the optimal working temperature of 152 °C. The inset of Figure 4b shows a magnified plot of the main figure for low H$_2$ concentrations (1–10 ppm). When H$_2$ was present, a noticeable peak occurred at about 10 s for various concentrations of H$_2$. We found that the Pd-SnO$_2$ NRs integrated with mini-GC was capable of detecting 1 ppm of H$_2$, as indicated in the inset of Figure 4b. As the concentration of H$_2$ increased, the height of a peak became larger. The change in the resistance was attributed to the sensing reaction of Pd-SnO$_2$ NRs with H$_2$, as described in Figure 2. As the H$_2$ concentration increased, the thickness of the depletion
layer becomes thinner due to the reaction of the $\text{O}_2^-$ and $\text{O}^-$ ions with the hydrogen atoms that decomposed on the surfaces of the $\text{SnO}_2$ NRs and Pd nanoparticles. However, the change in the resistance of the Pd-$\text{SnO}_2$ NRs was found to be changed without $\text{H}_2$ in ambient air. Figure 4c shows the change in the sensing signal of the Pd-$\text{SnO}_2$ NRs integrated with a mini-GC column for various $\text{H}_2$ concentrations at 152 °C. The change in the sensing signal was defined as $\Delta \log(R)$ according to Equation (1), and an increase was observed with an increase in $\text{H}_2$ concentration for the various $\text{H}_2$ concentrations (1–100 ppm) at 152 °C.

Figure 4. Sensing properties of the Pd-coated $\text{SnO}_2$ NR arrays using the mini-GC: (a) sensing response ($\Delta$ Sensor signal) to 100 ppm hydrogen as a function of operating temperature; (b) sensor signals of the Pd-coated $\text{SnO}_2$ NR arrays to various $\text{H}_2$ concentrations (1–100 ppm) at 152 °C (Inset: the cases of low $\text{H}_2$ concentration (1–10 ppm)); (c) sensing response as a function of $\text{H}_2$ concentrations at 152 °C.
In order to investigate the H\textsubscript{2} selectivity of the Pd-SnO\textsubscript{2} NRs integrated with mini-GC, we conducted measurements of the sensing signals for various gases in Pd-SnO\textsubscript{2} NRs and ZnO NPs integrated with mini-GC at their respective optimal operating temperatures. Figure 5a shows the sensor signals for H\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{3}COCO\textsubscript{3} in the ZnO NPs integrated with mini-GC. Figure 5b shows sensor signals for air, H\textsubscript{2}, N\textsubscript{2}, CO\textsubscript{2}, CH\textsubscript{4}, and CH\textsubscript{3}COCH\textsubscript{3} in the Pd-SnO\textsubscript{2} NRs integrated with mini-GC.

**Figure 5.** (a) Sensor signals for H\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{3}COCO\textsubscript{3} in the mini-GC integrated with ZnO nanoparticles (Inset: the cases of low H\textsubscript{2} concentration (50–1000 ppm); (b) sensor signals for air, H\textsubscript{2}, N\textsubscript{2}, CO\textsubscript{2}, CH\textsubscript{4}, and CH\textsubscript{3}COCH\textsubscript{3} in the mini-GC integrated with Pd-coated SnO\textsubscript{2} NR arrays.
In Figure 5a, the sensor signals of the ZnO NPs integrated with mini-GC were obtained upon exposure to 0.5% H\textsubscript{2} in synthetic air, 5% CO\textsubscript{2}, and 10 ppm CH\textsubscript{3}COCH\textsubscript{3} in N\textsubscript{2}. The sensing measurements were performed at the optimal operating temperature of 430 °C for the ZnO NPs integrated with mini-GC (see Figure S1 in Supplementary Material). The two peaks that occurred at about 13 s were observed in the sensor signals for 0.5% H\textsubscript{2} and 5% CO\textsubscript{2}, corresponding to the detection of H\textsubscript{2} and CO\textsubscript{2}, respectively. The curve for 10 ppm acetone in N\textsubscript{2} had two peaks, one at 13 s and one at 42 s. The first and second peak represented the emission of N\textsubscript{2} and acetone, respectively. The corresponding time of the second peak was consistent with the detection time of air-balanced acetone observed in our previous work [38]. In our mini-GC system, the target gas can be separated from the mixture gas due to the different strength of interaction between the gas molecules and the stationary phase in the packed column. The stationary phase in a GC column has a weak polarity. Therefore, due to their weak interaction, non-polar gases, such as H\textsubscript{2}, N\textsubscript{2}, and CO\textsubscript{2}, are released rapidly from the GC column. However, CH\textsubscript{3}COCH\textsubscript{3}, which is a polar gas, was released slowly. In this regard, H\textsubscript{2} is very difficult to detect selectively in the mixture of N\textsubscript{2} and CO\textsubscript{2} in the ZnO NPs integrated with mini-GC.

Figure 5b shows the sensing signals when the Pd-SnO\textsubscript{2} NRs integrated with the mini-GC was tested at 152 °C upon exposure to various gases, such as ambient air, 50 ppm H\textsubscript{2}, 5% CO\textsubscript{2}, 99.99% N\textsubscript{2}, 50 ppm CH\textsubscript{4}, and 50 ppm CH\textsubscript{3}COCH\textsubscript{3} in air. Only the sensor signal of 50 ppm H\textsubscript{2} had a noticeably large peak at about 10 s. There was no change in the resistance of the sensor when exposed to the other gases, because an operating temperature of 152 °C is too low to detect these gases, including carbon oxides and hydrocarbons. The results implied that the Pd-SnO\textsubscript{2} NRs integrated with the mini-GC had high selectivity for H\textsubscript{2} at 152 °C. According to the definition of the "Δ Sensor signal", the sensing response of the Pd-SnO\textsubscript{2} NRs to 50 ppm H\textsubscript{2} was estimated to be about 0.33 (Figure 5b), which was higher than the sensing response of 0.11 when the ZnO NPs were exposed to 0.5% H\textsubscript{2} (Figure 5a). In addition, the hydrogen sensing peak of the ZnO NPs at 50 ppm H\textsubscript{2} was difficult to distinguish from the baseline, as shown in the inset of Figure 5a. This indicates that the ZnO NPs cannot detect low hydrogen concentrations of <50 ppm. Therefore, the sensing performance of the Pd-SnO\textsubscript{2} NRs toward H\textsubscript{2} was shown to be significantly better than that of the ZnO NPs. The superior H\textsubscript{2} sensing property of the Pd-SnO\textsubscript{2} NRs was attributed to the synergistic effect of the catalyst and the height of the Schottky barrier, as described in Figure 2. Accordingly, the Pd-SnO\textsubscript{2} NRs integrated with the mini-GC had high selectivity and sensitivity for the detection of H\textsubscript{2} at the relatively-low working temperature of 152 °C.

We investigated the H\textsubscript{2} sensing performance of Pd-SnO\textsubscript{2} NRs integrated with mini-GC in a humid condition. Figure 6 shows the change of the sensor’s signal for various H\textsubscript{2} concentrations (1–100 ppm) at the highly humid condition of 90% relative humidity (RH) at 152 °C. All of the sensor signals for the different H\textsubscript{2} concentrations had a peak at ~10 s, corresponding the detection of H\textsubscript{2}. The intensity of the peaks became larger as the H\textsubscript{2} concentration was increased. These results were consistent with those obtained for H\textsubscript{2} in dry air (Figure 4a). The inset of Figure 6 shows the Δ Sensor signal of the Pd-SnO\textsubscript{2} NRs to various H\textsubscript{2} concentrations in dry and humid (90% RH) air. The results indicated that the sensitivity of the Pd-SnO\textsubscript{2} NRs was decreased at 90% RH, but the sensor was able to detect H\textsubscript{2} concentrations as low as 5 ppm at 90% RH.
To demonstrate the potential of the Pd-SnO$_2$ NRs sensor integrated with a mini-GC device for use in real-time monitoring, the performance of the manufactured sensing measurement system was evaluated using standard hydrogen gas. To determine the hydrogen content detected, the relation function between the $\Delta$ Sensor signal and H$_2$ concentration (Figure 4c) was utilized. Figure 7a–f shows the analysis process for measuring the concentration of the injected standard hydrogen gas. The measurement instructions were displayed on the front panel. After pressing the start button, a test gas of 10 ppm hydrogen was injected (Figure 7b). Gas sampling was performed for 20 s, and ambient air was used as the carrier gas (Figure 7c). After an analysis time of 100 s (Figure 7d,e), the system indicated that the concentration of hydrogen detected was 10.53 ppm (Figure 7f). Figure 8a–f shows the same analysis procedure for measuring the concentration of the hydrogen gas in exhaled breath; the results indicated that 9.66 ppm hydrogen was dissolved in the breath exhaled by the tester. This is consistent with several reports [45–47] that fasting basal hydrogen concentration in normal people’s breath is 8–10 ppm. According to the results, our study demonstrated that the manufactured hydrogen gas analyzer, which consisted of a Pd-SnO$_2$ NRs sensor and a mini-GC device, can rapidly and accurately detect hydrogen within 100 s; consequently, it should be utilized in analyzers for breath hydrogen testing.
Figure 7. Real-time hydrogen gas sensing test via the manufactured hydrogen gas analyzer, consisting of Pd-coated SnO$_2$ NR sensor and mini-GC, using 10 ppm of standard hydrogen gas. (a) Put mouthpiece in your mouth and press the start button, (b) Injection of a standard test gas of 10 ppm hydrogen, (c) Gas sampling for 20 s, (d) Starting gas analysis, (e) After 90 s of gas analysis, and (f) Display of the gas analysis result.

Figure 8. Real-time hydrogen gas sensing test via the manufactured hydrogen gas analyzer, consisting
of Pd-coated SnO$_2$ NR sensor and mini-GC, using tester’s exhaled breath. (a) Pressing the start button, (b) Blowing the exhaled breath for 12 s, (c) Gas sampling for 20 s, (d) Starting gas analysis, (e) After 90 s of gas analysis, and (f) Display of the gas analysis result.

4. Conclusions

We studied the sensing performance of a breath hydrogen analyzer based on a Pd-coated SnO$_2$ nanorods (Pd-SnO$_2$ NRs) integrated with miniaturized gas chromatography (GC) column. We found that the breath hydrogen analyzer was capable of measuring H$_2$ over a wide range of concentrations (1–100 ppm), within 100 s, at an optimal operating temperature of 152 $^\circ$C. We also found that the Pd-SnO$_2$ NRs could detect H$_2$ selectively in mixtures of interfering gases, such as CO$_2$, N$_2$, CH$_4$, and CH$_3$COCH$_3$. The higher performance of the Pd-SnO$_2$ NRs compare to the ZnO NPs for sensing H$_2$ was explained based on the catalytic effect and the reduction in the height of the Schottky barrier. Accordingly, we have summarized the meaningful advantages of our device as follows: smaller dimension (8 × 13 × 16 cm$^3$), lower cost, lower power (12 V), smaller sampling volume (1 mL), lower operating temperature (152 $^\circ$C), lower detection limit (1 ppm), and detection time (10 s).

This study is a first report on a prototype of a portable and compact breath-hydrogen-analyzer device, based on MOS sensors, such as Pd-SnO$_2$ NRs. The potential of the device as a breath hydrogen analyzer has been demonstrated by evaluating it with breath exhaled by a real human. More importantly, the device can selectively and sensitively detect trace amounts of hydrogen mixed in various VOC gases exhaled by humans.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/s22052056/s1, Figure S1: ∆Sensor signal of ZnO nanoparticles integrated into the mini-GC to 5000 ppm (0.5%) hydrogen as a function of operating temperature.

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