Hydrogen Sensors Based on Flexible Carbon Nanotube-Palladium Composite Sheets Integrated with Ripstop Fabric

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ABSTRACT: This work describes the design and fabrication of free-standing carbon nanotube-palladium (CNT-Pd) composite sheets for hydrogen gas sensing. The CNT-Pd composites were made by electroplating palladium onto a solvent-densified and oxygen plasma-treated CNT sheet. The latter was prepared using high purity CNTs drawn from a dense, vertically aligned array grown by chemical vapor deposition on silicon substrates. The CNT-Pd sheets were characterized by energy-dispersive spectroscopy, scanning electron microscopy, and X-ray diffraction. The amount of palladium in the composite was 16.5 wt % as measured via thermogravimetric analysis. Thin strips of the CNT-Pd sheets were assembled as chemiresistor sensors and tested for hydrogen gas detection. The sensors demonstrated a limit of detection of 0.1 mol % and displayed signal reversibility without the need for oxygen removal or heat treatment. A decrease in signal reversibility was observed after multiple exposure cycles; however, redensification with ethanol significantly restored the original reversibility. The sensor showed the Freundlich adsorption isotherm behavior when exposed to hydrogen. The material’s potential application toward a wearable, flexible sensor was demonstrated by integrating the chemiresistor onto a fabric material using hot-press processing and testing the composite for hydrogen sensitivity.

1. INTRODUCTION

Recent decades have seen a diversification in the utilization of hydrogen gas used for industrial and research applications. Hydrogen is employed as a fuel source in both space exploration and fuel cells and is also currently being investigated for use in medical applications.1,2 Additionally, it is used for heat treatment of metals, the refinement of heavy crude oil,3 and in the semiconductor processing technologies. Hydrogen can also be produced as a byproduct of nuclear power plants4 and coal gasification.5 Recent advances in hydrogen-storage capabilities also increase the potential of hydrogen as an environmentally friendly alternative to fossil fuels for cars and trucks.6–9 One important issue, however, is that hydrogen poses a serious safety hazard in these scenarios because of its odorless, colorless, and flammability (4 vol % lower explosive limit and 75 vol % upper explosive limit).10 Therefore, developing versatile hydrogen sensors is essential, especially sensors for personal use.

Palladium has frequently been used for sensing hydrogen via changes in its mechanical and electrical properties because of its ability to absorb vast quantities of hydrogen gas. The interstitial spacing of the Pd crystal structure, as well as the presence of two empty electron d-orbitals, allows for both the dissociation of molecular hydrogen into atomic hydrogen and its absorption into palladium.11–13

Carbon nanotubes (CNTs) have received wide attention for a variety of applications because of their remarkable properties since first reported by Radushkevich14 and Iijima.15 In particular, CNTs have been found to have high electrical and thermal conductivity, strong mechanical properties,16,17 and the ability to be functionalized covalently18–21 and non-covalently.22–26 Chemical vapor deposition (CVD) has been proven to be effective at growing arrays of vertically aligned CNTs that allow for a property called “spinnability”, which facilitates easy macro-assembly of CNTs into either sheets or threads in a simple and scalable fashion.27–29 The CNTs from these “spinnable” arrays are easier to process, adapt for larger scale production, and are essentially free of residual catalyst materials.30

CNTs have also been explored for potential use in gas-sensing applications.31–34 One notable sensor application of CNTs is the chemiresistor, a conducting element that changes its electrical resistance as it is exposed to a target gas. CNTs that have not been chemically or physically functionalized (pristine CNTs) are electrochemically active because of the presence of π electrons surrounding the carbon backbone.

Received: September 16, 2019
Accepted: December 9, 2019
Published: December 23, 2019

DOI: 10.1021/acsomega.9b03023
ACS Omega 2020, 5, 487–497

Supporting Information

Cite This: ACS Omega 2020, 5, 487–497

http://pubs.acs.org/journal/acsodf

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Electron-withdrawing molecules can attract these π electrons away from the CNT conductive band, altering the CNT electrical conductivity. However, this electrochemical activity of pristine CNTs is weak for many gaseous analytes making it difficult to distinguish between different electrochemically active gases. Therefore, many researchers have opted to use CNTs as a scaffold for functionalization with more strongly electrochemically active materials, such as palladium (CNT-Pd), to enhance their hydrogen-sensing capabilities.

However, many of these sensors have practical disadvantages, such as requiring oxygen to reverse or recuperate the sensor after hydrogen gas exposure and also a lack of durability and mechanical flexibility.

Spinnable CNT arrays have been used to design and fabricate hydrogen sensors. The ease of obtaining CNTs from spinnable arrays into useful sensor structures gives them an advantage over other similar materials such as ZnO nanotubes, which must be grown directly on a sensor structure or applied via other means. Yan et al. reported a sensor consisting of 1–5 layers of CNT ribbon capable of reversibly detecting hydrogen concentrations over a range of 0.5–10% and achieving response times under 200 s. In another paper, continuing their work, Yan et al. adhered 2–6 layers of CNTs from a spinnable array to Au electrodes and used electron-beam evaporation to deposit palladium on the CNTs. The sensor was able to detect hydrogen over a range of 0.5–10%. Kim et al. used two layers of CNT ribbon on Au/Cr electrodes and achieved a low detection range of 0.0002% (2 ppm)–0.1% (1000 ppm) with response times of above 6 min at 2 ppm to less than a minute for 1000 ppm. Han et al. tested a CNT-Pd-based sensor over a hydrogen concentration range of 3–35%. The sensor from this group was fabricated by drawing from spinnable CNT arrays and depositing several layers of CNT ribbon onto a polymer substrate. A key similarity in the references mentioned previously is that very thin CNT sheets, with a thickness less than a micron, have been used. This precludes them from performing as a free-standing structure and requires a substrate support. The primary motivation for this work was to design and create hydrogen sensors based on CNT sheets with an appreciable thickness that allowed them to perform as free-standing structures.

A potential way to implement a CNT-based sensor, especially for personal gas-sensing applications, is by integrating the CNT-Pd sensors into wearable fabrics. Fabric-integrated sensors provide key advantages over conventional sensors such as flexibility and ability to be fabricated in a variety of geometries for personal monitoring. Interest in this topic has produced a plurality of fabric-integrated sensors for different analyte gases and a range of methods to integrate the sensing element into the fabric, including printing, embroidery, thin-film deposition, weaving conductive fibers into a fabric mesh, and depositing sensing materials directly onto the fabric. However, these techniques have revealed drawbacks that limit their implementation. Printed materials are vulnerable to mechanical damage, embroidered and woven materials can suffer harm during their fabric integration, and thin-film materials (i.e., prepared by sputtering) require a specialized and expensive vacuum environment. More versatile integration techniques are needed in order to increase the viability of fabric-integrated sensors.

In this work, a simple and scalable method that can be conducted in an ambient environment, involving atmospheric plasma treatment followed by ethanol densification and electrolss and electroplating Pd deposition, is presented for fabricating free-standing CNT-Pd sheet composites for use as a chemiresistive hydrogen sensor. The sensor created in this way maintained its sensing capabilities after being successfully integrated into a fabric by employing hot-pressing and polyvinyl alcohol (PVA) as an adhesive. The change in electrical resistance of the obtained composite sheet was found to be reversible for H₂ sensing but lost this property after several test cycles of hydrogen gas exposure. Redensifying the sheet with ethanol significantly contributed to restoring its reversibility. Scanning electron microscopy (SEM) was used to study the morphology of the composites. Energy-dispersive spectroscopy (EDS) and X-ray diffraction (XRD) were conducted to identify the components of the composite. In order to determine the metal content of the composite sample, thermogravimetric analysis (TGA) was practiced.

2. EXPERIMENTAL SECTION

2.1. Materials and Equipment. Spinnable CNT arrays were grown in-house using a previously reported CVD technique. Oxidized single crystal silicon (CAS no. 7440-21-3, procured from SQI Inc, semiconductor grade) wafers with a 5 nm buffer layer of alumina and 1.2 nm double layer of iron (CAS no. 7439-89-6) and cobalt (CAS no. 7440-48-4) on top were sputtered onto the wafer to act as a catalyst for CNT growth. The gas mixture utilized during the CVD process consisted of the following gases, with the purity greater than 4 N and represented by their partial pressure: 560 mmHg argon (CAS no. 7440-37-1, Wright Brothers Inc.), 60 mmHg H₂ (CAS no. 7439-89-6) and 140 mmHg iron (CAS no. 1333-74-0, Wright Brothers Inc.), and 140 mmHg ethylene (CAS no. 74-85-1, Gas Innovations). The hydrocarbon served as a carbon precursor. Simultaneously, water vapor was added in the gas mixture with a concentration of 900 ppm to accelerate the growth kinetics of the CNTs. Pressure was kept at a total pressure of 1 atm and the temperature was maintained at 750 °C. Palladium chloride (99%) (CAS no. 7647-10-1) was purchased from Sigma-Aldrich and used for electrolss deposition followed by electrod deposition on the CNT sheet. Stannous chloride dihydrate (98.2%) (CAS no. 7772-99-8), used as a reducing agent during electrodeposition, was procured from Fisher Scientific. Thirty-six normality (18 M) sulfuric acid (CAS no. 7664-93-9) with a listed purity of 95–98 wt % was purchased from Fisher Chemical. Fifty micron-thick Buckypaper, consisting of single-walled CNTs, was employed as a substrate in the CNT sheet-manufacturing process and was provided by General Nano LLC. A gas mixture of ultrahigh purity 5 wt % hydrogen in argon and, separately, prepurifed argon as a diluent gas, was purchased from Wright Brothers Inc and used in the hydrogen-sensitivity experiment. PVA (CAS no. 9002-89-5), utilized for fabric integration, was a medium molecular weight substance, 86–89% hydrolyzed, and purchased from Alda Aesar. The military grade Ripstop fabric for the CNT sheet integration was a polyester blend provided by the US Army Research Lab (ARL).

Atmospheric pressure plasma treatment of the CNTs was performed using a Surfax Technologies Atomfl instrument, model 400 with an AH-250D circular torch. Raman spectroscopy was conducted with a Renishaw inVia Raman instrument. Contact angle measurements were performed with a Kruss Scientific DSA25E Drop Shape Analyzer. Gas flow rates were controlled using MKS model 1259-C mass flow controllers.
reduced by SnCl₂ to elemental Pd, thus decorating the surface. Solution of SnCl₂ in order to wet the surface with the Sn salt. Deposition of Pd involves exposing a substrate to aqueous Te after plasma treatment and Pd deposition. While still on the ease with which the CNT sheet could be removed from it a substrate because of its flexibility, electrical conductivity, and the ease with which the CNT sheet could be removed from it after plasma treatment and Pd deposition. While still on the Teflon cylinder, the sheet was then exposed for 1 min, at a rate of 3.5 s/rotation, to 100 W atmospheric helium/oxygen plasma in order to enhance CNT interaction with the aqueous palladium chloride solution. This has been achieved because of the increased hydrophilicity of the CNT sheet after plasma treatment. The sheet was then densified with ethanol and allowed to dry.

Electroless deposition was utilized in order to aid with palladium deposition and produce reversible sensor samples more reliably. The procedure was based on the one described in patent no. 1,921,941. The first step of electroless deposition of Pd involves exposing a substrate to aqueous solution of SnCl₂ in order to wet the surface with the Sn salt. Then, the same substrate is exposed to PdCl₂, which gets reduced by SnCl₂ to elemental Pd, thus decorating the surface of the substrate with Pd particles. They later act as sites for electrodeposition of palladium. Such a process enhanced a procedure enabled decoration of the CNT sheet with a brush electroplating technique, which is based on the work previously done by this group, is used for electrodeposition of Pd from the PdCl₂ electrolyte. In this work, a 0.22 M solution of SnCl₂ was transferred via a pipette onto the CNT sheet and remained there for 10 s, followed by rinsing with water. Next, the sample was exposed, in the same manner, to a 0.01 M PdCl₂/0.36 M H₂SO₄ solution for 10 s, again followed by rinsing with water. This procedure enabled decoration of the CNT sheet with a network of Pd clusters. Following the electroless deposition step, a modified “brush” electrodeposition technique, which is based on the work previously done by this group, is used for the electrodeposition of palladium. Such a process enhanced a uniform electroplating of a Pd film on the Pd-decorated CNT sheet. The “brush” setup is briefly described here. A cotton medical gauze is wrapped around a flattened end of a steel tube. A Teflon mesh is used to ensure that the gauze does not adhere to the CNT sheet. The gauze was soaked in the same 0.01 M PdCl₂/0.36 M H₂SO₄ solution that was used for electroless deposition. A 3 V potential was applied to deposit Pd film, running for 60 rotations where each rotation took 3.5 s. The brush electroplating setup is depicted in Figure 1. Once the electroplating is complete, the CNT-Pd sheet is removed from the Buckypaper substrate. Deposition of Pd was confirmed with SEM, EDS, and XRD. The amount of Pd in the CNT sheet was evaluated using TGA.

2.2. CNT Sheet-Making Procedure and Characterization. CNT sheets were prepared by wrapping 100 layers of CNT ribbon from a spinnable array around a Buckypaper substrate on a Teflon cylinder, in a manner similar to a previously published work. Buckypaper was used as a substrate because of its flexibility, electrical conductivity, and the ease with which the CNT sheet could be removed from it after plasma treatment and Pd deposition. While still on the Teflon cylinder, the sheet was then exposed for 1 min, at a rate of 3.5 s/rotation, to 100 W atmospheric helium/oxygen plasma in order to enhance CNT interaction with the aqueous palladium chloride solution. This has been achieved because of the increased hydrophilicity of the CNT sheet after plasma treatment. The sheet was then densified with ethanol and allowed to dry.

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2.3. Gas-Sensitivity Testing Setup. Gas-sensitivity testing was conducted using a custom-made system for electrical measurements, integrated with a gas exposure chamber. The chamber had an inlet valve for the analyte gas (hydrogen) and a bifurcated outlet line. One line of the outlet went to a vacuum pump and the other was connected to a bubbler that led to the exhaust. To prepare the sample for hydrogen exposure, the chamber went through a 30 min period of vacuum evacuation followed by 30 min rinsing with argon flow. This procedure was repeated one more time to secure a clean environment. The sample was then exposed to various concentrations of hydrogen gas mixed with argon. The H₂ concentration was set and controlled by MFCs. The flow rate ratios were varied between a 51 mol % (5 wt %) H₂ in Ar and pure Ar acting as a diluent gas.

2.4. Fabric Integration with the CNT Sheet. CNT-Pd sheet integration into the Ripstop fabric was achieved by partially soaking the fabric in an aqueous PVA solution. The solution was mixed in a ratio of 1 g of the polymer to 20 mL of water. The sheet was laid on top of the soaked fabric area and compressed for 15 min at a temperature of 104 °C and 30.8 metric tons using a hot press.

3. RESULTS AND DISCUSSION

3.1. Effect of Oxygen Plasma on the CNT Sheet. Raman spectra of the CNT sheet show an increase in the ratio of the D (1347 cm⁻¹) to G (1582 cm⁻¹) peak (I_D/I_G) after plasma exposure, as seen in Figure 2a. Our previous work has demonstrated the effects of oxygen plasma on CNTs. Exposure to high-energy oxygen plasma results in the breaking of graphitic sp² bonds (represented by the G peak) and forming of defect sites that are composed of sp³ bonds (represented by the D peak). Thus, an increase in the I_D/I_G ratio represents an increase in sp² defect sites. The presence of oxygen in the plasma results in the formation of polar oxygen-based functional groups typical for alcohols and carboxylic acids at these defect sites. The addition of these polar functional groups aids in the CNTs’ hydrophilicity as can be seen when comparing contact angle measurements of pristine and plasma-functionalized CNT sheets, as demonstrated in Figure 2b–d.

3.2. SEM and EDS of the CNT-Pd Sheet. The images as shown in Figure 3a,b represent the presence of nanoparticles that are evenly distributed throughout the sheet, thus decorating the CNT bundles. Figure 3a illustrates the side closest to the anode and Figure 3b reveals the side closest to the cathode.
the cathode. Both figures prove a lack of significant particle size gradient. The spherical nanoparticles, which represent clusters of Pd atoms, have an average size of 71.7 nm with a standard deviation of 14.8 nm, based on measurements taken from Figures 3a,b. A cross-sectional image of the CNT-Pd sheet is shown in Figure 3c. It confirmed that palladium nanoparticles have been formed throughout the thickness of the CNT sheet, although the majority of Pd deposition was observed on the surface exposed directly to the electrolyte. Further cross-sectional imaging showed the average thickness of the sheet to be 4.5 μm with a standard deviation of 0.4 μm. The results from the EDS analysis are presented in Figure 3d. They confirmed that the observed particles are palladium. Residual tin from the electroless deposition was also detected along with carbon from the CNT sheet. Oxygen was also present; however, this was due to the effect of plasma-functionalizing the sheet with oxygen functional groups.

3.3. XRD of the CNT-Pd Sheet. XRD results are presented in Figure 4. They show a (002) broad peak at 25.5°, which is attributed to CNTs [JCPDS card no. 00-085-1638]. Two additional narrow peaks occur at 40.3 and 47.0°. These two peaks are consistent for the known spectrum of Pd (JCPDS card no. 00 046 1043). The relatively thin nature of the CNT-Pd sheet leads to increased noise in the XRD spectra, which explains why other weaker peaks associated with Pd are not apparent.

It has been reported that SnO₂ does have hydrogen-sensing capabilities.61,62 The XRD spectrum of SnO₂ has a distinct peak at 51.8° [JCPDS card no. 00-041-1445]. The lack of any peak at this angle as shown in Figure 4, with no other peak nearby to potentially obscure it, indicates that SnO₂ is not present in the sheet in any significant amount. Thus, it is not feasible to expect that any hydrogen sensitivity of the fabricated sensor is due to the presence of SnO₂.

3.4. TGA of the CNT-Pd Sheet. The obtained thermogram as shown in Figure 5 represents a residual mass of 16.5 wt %. This residual mass constitutes the weight of the palladium component of the CNT-Pd sheet. Thermogravimetric behavior of CNTs has been well-documented.63−65 For the first derivative measurement, the minimum that occurs at 640 °C represents the main portion of Pd combusting, while the slow decline in mass preceding this minimum is the result of the volatile material, such as water vapor, residual solvent, polymers, and amorphous carbon being driven off. It is reasonable to believe that Pd oxidizes during the TGA procedure. However, PdO reverts to Pd metal and oxygen.
upon being heated above 900 °C. This motivated us to conduct TGA of our samples up to 1200 °C, where the residual mass is expected to represent only the Pd metal. This decomposition explains the slight decline in mass occurring at 815 °C.

3.5. Hydrogen-Sensitivity Measurements with the Fabricated CNT-Pd Sensor. As mentioned earlier, the fabricated CNT-Pd sensor was tested by exposing it to hydrogen with different concentrations and simultaneously measuring the electrical resistance of the device. Three minutes after initial exposure to H₂, a rapid decline in the resistance was observed, as shown in Figure 6a. This decline continued for approximately 25 min, and then a new resistance baseline was established. From this baseline, the electrical resistance rose to a new level when exposed to higher concentrations of hydrogen and declined when the concentration was lowered back to the previously used value. The initial decline in resistance is due to expansion of the Pd particles in the sample. During the transition of palladium to palladium hydride, changes in crystal conformation result in a unit cell expansion of 3.5%, with some dimensional changes of the particles reaching up to 14%. With enough palladium present, this expansion causes palladium particles to form new and improved connections with other Pd particles and creating a more conductive network with a favorable electron pathway in the sample. After this initial exposure to H₂ and linking of palladium particles, further particle expansion pushes CNT bundles in the sheet structure apart, increasing the overall electrical resistance of the material. This can be clearly seen at the 10 min mark in Figure 6b, where the resistance begins to increase by 0.86%. This mechanism is relatively slow as the increase starts to occur 5 min after hydrogen exposure begins. In contrast to the previous mechanism, the changes in electrical resistance that corresponded to variation in the hydrogen concentration occurred on the timescale of seconds, implying a second mechanism based on the surface phenomenon. Several previous studies have discussed the surface interactions of palladium hydride with CNTs. When
palladium transitions to palladium hydride, a lowering of the work function occurs, this results in electrons being more readily transferred to the CNTs, which has been theorized to fill p-type conductors in the CNT sheet and therefore increase the electrical resistance of the CNT-Pd composite.

One feature of the fabricated sensor is that the electrical resistance decreases as the hydrogen concentration is lowered, despite there being no oxygen to remove the hydrogen from palladium. Such a resistance behavior is illustrated in Figure 6a at the 35, 40, 45, and 65 min marks and in Figure 6b when the H₂ concentration is lowered at the 35 min mark. This can be explained by the thermodynamic properties of the hydrogen-palladium system. Changes in the partial pressure of hydrogen (i.e., the concentration of hydrogen in the surroundings) can cause desorption from the palladium with smaller particles resulting in better desorption capabilities. If the concentration of hydrogen in the surroundings decreases, hydrogen will desorb from the palladium in order to re-establish equilibrium. However, the initial desorption is only partial, with total desorption taking some time to be achieved. This factor explains the behavior of the gas sensor presented here, with the concentration of hydrogen in the gas mixture exerting an influence on the content of H₂ in the solid palladium mixture.

After several repeated hydrogen exposure cycles, however, the property of the signal reversibility declined, as displayed in Figure 6c. This can be attributed to the palladium clusters becoming more saturated with hydrogen after repeated testing. Another mechanism that accounts for this is that repeated expansion of the Pd particles can result in the CNT structure being pushed away and partially detached from the particles. This, in turn, can result in the CNT bundles being less responsive to changes in the surface behavior brought about by the transition of palladium to palladium hydride. Using ethanol to redensify the sample helped to mitigate such an effect, as can be seen in Figure 7. Densification brings the CNT bundle structure back into close contact with the Pd particles.

Exposing the CNT-Pd sheet to different concentrations of hydrogen, punctuated by periods of flushing argon-only flow, resulted in the formation of distinct signal peaks. The height of each peak was proportional to the concentration of hydrogen being used with the sample showing a distinct response to concentrations as low as 0.1 mol %, which is illustrated in Figure 8a,b. From these peaks, a calibration curve of percent change in resistance versus hydrogen concentration is plotted in Figure 8c. This calibration curve obeyed a Freundlich absorption isotherm fitted with an equation of $y = 0.40039 - \frac{x}{0.01021}$

Figure 6. Change in electrical resistance of the CNT-Pd sheet with time when exposed to hydrogen: (a) initial exposure, (b) after two hydrogen exposure cycles, and (c) after six hydrogen exposure cycles.

Figure 7. CNT sheet resistance response to 0.3% hydrogen exposure before and after ethanol redensification. The sheet previously endured seven hydrogen exposure cycles.
with $R^2 = 0.98982$. Based on this assumption, a linear calibration line could be obtained by plotting the log of both axes, as shown in Figure 8d. The equation for this line was $0.34928x - 0.37999$ with $R^2 = 0.97908$. The time needed for the sensor to reach 90% of its reading signal is known as the response time. This sensor parameter showed an exponential relation to hydrogen concentration for our device as demonstrated in Figure 8e. The exception to this was the 163.2 s response time for 0.1 mol % hydrogen. Concentrations in the range of 0.6–4.6 mol % showed an average response time of 91.90 s and higher concentrations of 6.0 mol % and 8.5 mol % revealed a response time of 184.8 and 306 s, respectively. The relatively high response time for 0.1 mol % followed by a decline in the response time is expected and is similar to what has previously been reported.38,42,43,74 However, this work differs from the literature in that there is an exponential increase in response times at higher concentrations. A possible explanation for this divergence from the literature is the thickness of the sheets. Yan et al.44 tested a very thin CNT-Pd sheet of 1–5 layers. They found that the five-layer sample was the only one to show a distinct increase in the response time at higher concentrations. In this work, 100 layers within the sheet with a total thickness of about 4 μm were accumulated and utilized in order to make a more stable material, so it is plausible that the increased number of layers would further exacerbate the rise in response times at higher concentrations.

Ripstop fabric integration conducted as per the procedure described earlier was successful, as displayed in Figure 9a. The CNT-Pd sheet remained intact even after bending (Figure 9b). The mechanical and electrical stability of the sheet was further demonstrated by subjecting a sample to repeated bending for 350 000 cycles. Upon this test, the electrical resistance of the sheet was measured and found to have increased by only 1%. A snapshot of the video illustrating the CNT-Pd sheet going through the bend testing is shown in Figure S9 of the

Figure 8. Results from variety of tests performed with the created CNT-Pd sensor exposed to H₂: (a) signal peaks for 0.1, 0.6, 1.2, 1.8, 2.4, and 8.5 mol % hydrogen gas, (b) signal peaks for 3.2, 4.6, and 6.0 mol % hydrogen gas, (c) Freundlich calibration curve showing the change in resistance vs hydrogen concentration, (d) linear calibration curve showing the log of the change in resistance vs log of hydrogen concentration, and (e) response time vs hydrogen.
standing and utilizes CNTs as the built-in current collector, it can be applied in a variety of settings, such as fabrics, with relative ease. Samples consisting of 100 CNT layers were selected for the final assembling of the CNT-Pd sheet because such a number provided satisfactory balance between the minimum material used and a stable and handleable substrate for palladium deposition. As mentioned in Sections 3.1 and 3.2 of this work, the plasma functionalization and palladium deposition are predominately surface treatments and therefore may not benefit from additional CNT layers in the sample. Utilizing additional CNT layers may also be a detriment to the sensing capabilities, as adding too much CNTs to the composite might normalize and dominate the electrical conductivity of the entire sensor, resulting in less electrical current passing through the palladium-enriched surface layer and therefore the transition to palladium hydride may be less noticeable. The inherited flexibility of the sensor reported here is also an improvement over other reported similar devices in the literature. The used approach for fabricating the sensor in this work via simple electrochemical deposition adds to the manufacturing advantages especially when comparing the manufacturing techniques described in the literature. Most of the hydrogen sensor fabrication techniques reported in the public domain include sputtering, E-beam evaporation, thermal evaporation, and atomic layer deposition (ALD) of palladium. These methods require a vacuum environment and complex and expensive equipment. The advantage of the sensor fabrication method detailed in this work is that it can be entirely conducted at atmospheric pressure, making scale-up much more possible. An additional advantage is the processing time to deposit palladium. Compared with ALD, which is more time-consuming, the electrochemical method practiced in this work deposits the necessary amount of palladium in a much quicker process. Although electrodeposition was also previously used for Pd deposition, it is often implemented in a way that is not amenable to scale-up. This work demonstrates improvement upon the conventional electrochemical deposition method by allowing easy scale-up and continuous roll-to-roll processing. Previously reported sensors have achieved higher sensitivity reaching down to 2 ppm (0.0002 mol %), as a result of utilizing an extremely thin and fragile CNT material, which is not appropriate for free-standing devices. We believe that this work demonstrated a scalable and inexpensive method to produce a free-standing and flexible material, sensitive to hydrogen and capable of integration into fabric structures.

4. CONCLUSIONS

This work demonstrates a scalable process for fabricating a CNT-Pd sheet used as a fabric-integrated gas sensor. The method can ideally be used for producing bulk hydrogen-sensing material. The free-standing Pd-decorated CNT sheet was tested for hydrogen gas sensitivity by monitoring the change in electrical resistance via a four-probe setup. It was shown that upon initial exposure to hydrogen, the resistance of the sheet declines followed by displaying a high sensitivity to changes in the concentration of hydrogen. The electrical resistance of the sample increased as the hydrogen concentration increased and decreased when the hydrogen concentration was lowered. The CNT-Pd sheet could detect concentrations of hydrogen as low as 0.1 mol %. After several tests, the reversibility of the sheet signal declined. Redensi-
cation of the sheet with ethanol significantly restored sensor reversibility. A calibration curve for the CNT-Pd sensor was generated fitting a Freundlich adsorption isotherm. The sheet was integrated into a fabric material using a hot-press method and this processing did not change the sensitivity of the obtained sensor toward hydrogen exposure. In this case, the fabric-integrated sensor lost the previously observed reversibility because of the porous nature and rough structure of the fabric and because of the PVA infiltration into the CNT sheet structure. Potential future directions for this research entail improvement of the fabric-integrated sensors using a variety of fabric materials and interfacing polymers and the detection of other target gases.

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