Pd Nanoparticle Film on a Polymer Substrate for Transparent and Flexible Hydrogen Sensors

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ABSTRACT: Alongside the rise in fully automated equipment and wearable devices, there is currently a high demand for optically transparent and flexible gas sensors operating at room temperature. Nanoparticle films are ideal H$_2$-sensing materials that can be coupled with flexible substrates because of their discrete nanogranular structure and unique interparticle electrical responsiveness. In this work, we present an optically transparent and flexible H$_2$ sensor based on a Pd nanoparticle film, prepared on a polyethylene terephthalate sheet using a straightforward nanocluster deposition technique. Hundreds of bending cycles demonstrated that the sensor has good electrical stability and mechanical robustness without significant degradation in H$_2$-sensing performance. The H$_2$-sensing behaviors under bent state were systematically evaluated. The loading of tensile and compressive strains under bent state produced a positive and negative influence, respectively, on the sensing performances. The possible influence mechanism of the tensile and compressive strains on the H$_2$-sensing performance was attributed to the changes in the percolation network topology and the interparticle space induced by the strains. The ability to detect a H$_2$ concentration as low as 15 ppm, dynamic response range as wide as 0–10%, and sub-10 s response time was achieved. In addition, the sensor can be operated in the relative humidity range of 0–90% at room temperature. These results demonstrate that the sensor exhibits significant potential for next-generation transparent and flexible H$_2$ detectors.

KEYWORDS: palladium nanoparticle, flexible, transparent, hydrogen gas sensor, nanogranular

INTRODUCTION

Hydrogen energy, as the most promising and one of the cleanest new alternative energy sources, has attracted unprecedented interest over the last few decades. However, hydrogen gas (H$_2$) is colorless, odorless, and flammable at concentrations above 4% in air. Because of the high risk of explosion, H$_2$ sensors have an essential role in the development of hydrogen economy. Studies of H$_2$-sensing materials have various applications, such as in medical devices, civilian or military sensors, consumer electronics, and energy devices. Chemical sensor devices on flexible substrates have also been increasingly reported. By coupling nanostructured materials with flexible substrates, these devices show a range of advantages, including a relatively simple fabrication process, cost effective manufacturing, extreme portability, and good wearability. The H$_2$ sensors were also involved in the development of flexible wearable electronics because of their potential to be integrated into various smart wearable devices for healthcare applications. For instance, the H$_2$, produced by intestinal bacteria, coexist in the breath gas. A wearable H$_2$ sensor provides a potentially cheap way for medical examination such as evaluation of colonic flora by detecting and analyzing the H$_2$ concentration in human breath. Furthermore, another current trend is to make gas sensors...
Because of the enhanced chemical activity and shortened diffusion path of the interstitial hydrogen atoms within the Pd hydride induced by the decrease of the dimension and size of materials. Moreover, it is fortunate that both transparency and flexibility of the devices can be achieved by nanostructuring the sensing materials. Therefore, nanostructured materials are well-suited for manufacturing the flexible and transparent sensors.

In this work, we report the fabrication of a flexible, optically transparent, and resistive type H2 sensor using Pd nanoparticles (NPs) as the sensing active material and polyethylene terephthalate (PET) as the substrate. To achieve light transmittance and flexibility of our H2 sensors we controllably deposited Pd NPs on PET substrates, forming random percolative NP films with a transmittance of above 80% in the visible region of the spectrum. Because of the discontinuous granular architecture, the existing nanogaps between the closely spaced Pd NPs resulted in the HILE-based sensing behavior. As a flexible gas sensor, subjected to hundreds of bending cycles, our sensor showed great tolerance toward repeated bending, good electrical stability, and mechanical robustness without significant degradation in the H2-sensing performance. The influence of tensile and compressive strains under bent state on the H2-sensing performance was systematically evaluated. Interestingly, a tensile strain applied induced enhanced the H2-sensing performance with respect to the response amplitude, sensitivity, and response speed. The possible mechanism was attributed to changes in the percolation network topology and the interparticle space induced by the strains. The ability to sense H2 concentrations as low as ~15 ppm, dynamic response range as wide as 0–10% and a sub-10 s response time were achieved. In addition, the sensor can be operated in the relative humidity (RH) range of 0–90% at RT.

RESULTS AND DISCUSSION

Sensor Fabrication and Characterization. Briefly, the preparation process for the transparent and flexible H2 gas sensor in our research was similar to that in our earlier contributions. A PET sheet with prepatterned interdigital
electrodes (IDESs) prepared by mask evaporation deposition (Figure 1a,b) served as the flexible substrate. As shown in Figure 1c, a magnetron plasma gas aggregation cluster source was employed to generate the Pd NPs. A Pd NP film with well-controlled NP coverage of the flexible substrate was achieved by in situ monitoring the current across the IDE gap by a computer-interfaced sourcemeter (Keithley 2636B). A typical current evolution of the NP arrays at a bias of 1 V, which can be described by the percolation model, as a function of deposition time is shown in Figure S1. During the deposition process, the NPs produce a circular deposit on the substrate, its thickness being larger in the center. For fabricating the sensors efficiently, the PET substrate should be placed near the section center of the cluster-beam spot as possible as it can be.

Representative high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the Pd NP film, which was prepared by depositing Pd nanoclusters at a deposition rate of 0.2 ± 0.05 Å/s for ~8 min, are shown in Figure 2a. From the high-magnification STEM image, it is clearly seen that the Pd NPs are predominantly cuboid, which corresponds to face-centered cubic structures. The Pd NPs were closely packed and formed a discontinuous film in a disordered manner. Although a large number of NPs were in contact with each other in the NP aggregation areas, the high-resolution STEM (HRSTEM) image (Figure S2) clearly shows that these neighboring NPs did not coalesce to form larger metallic islands or a continuous film, but maintained their own individual shapes and/or formed interfaces between adjacent NPs. As a result, these individual NPs and aggregates formed numerous electron-conducting pathways based on percolation in the flexible substrate. We stochastically captured eight TEM images at different areas of this sample at low-magnification, as shown in Figure S3, for statistical analysis of the size distribution of the NPs. The diameters of the NPs were measured from these TEM images one by one, and the statistical results are shown in Figure 2b. The size distribution of NPs fitted a log-normal dependence with a probable size of ~7.2 nm.

To confirm that the same morphology is always present in the flexible PET substrate, scanning electron microscopy (SEM) characterization of the Pd NP film on the PET substrate was carried out. Figure 2c is the SEM image of the Pd NP film on the PET substrate that was prepared simultaneously with the sample on the copper TEM grid. This image shows that the Pd NP film on the PET substrate exhibits nonuniform-like morphology that is consistent with the microstructure observed in the sample on the copper TEM grid, although it is difficult to achieve high-quality SEM images at high magnification because of the high electric insulation of the PET sheet.

Pd is widely used to detect and quantify H₂ concentration because of its specific interactions (catalytic surface reactivity and solubility) with H₂. However, bulk metal Pd is susceptible to mechanical damage originating from volume changes associated with repeated H₂ absorption and desorption. On the basis of the above microstructure characterization (Figure 2a,c), Pd NP films obtained by reducing the size and dimensions of the bulk metal can be assembled to form a granular film—an artificial material with unique electronic properties. The individual grain-like nanostructure endows the Pd NP films with the ability to withstand mechanical deformation, which makes the Pd NP films that can be used as a flexible H₂-sensing element. A further advantage of Pd NP films is superior H₂-sensing performance owing to their increased surface-area-to-volume ratio.

To ensure the transparency, three samples were prepared on PET substrates with different deposition times of 2, 4, and 8 min at a deposition rate of 0.15 ± 0.05 Å/s, and their TEM images and transmittances from visible to near infrared wavelength region (400–1500 nm) are showed in Figure S4. The experimental details are provided in Figure S5 in the Supporting Information. We observed that longer deposition time a induced drop in transmittance. Within the visible wavelength region (400–800 nm), the transmittance slightly increased with an increasing wavelength, as seen in Figure 2d. At 550 nm, the transmittance of the sample with a deposition time of 8 min was above 86%. The high transmittance of the Pd NP film-based H₂ sensor emerge from the submonolayer structure composed of metal NPs because of its extremely thin thickness. Here, light absorption of the Pd NP films induced by plasmon resonance was not observed in the visible wavelength region. The inset of Figure 2d shows the photograph of a Pd NP film on a PET sheet with a university badge as the background. The high transmittance of the Pd NP film allows its practical applications as gas sensors integrated with other optical devices.

**Electrical Stability and Repeatability of the H₂ Sensor.** Electrical stability and mechanical robustness are of extreme importance in a number of practical applications, such as wearable and portable electronic devices to detect flammable and combustible gases in the ambient atmosphere, especially for a flexible gas sensor. To evaluate the reliability of the H₂ sensor and the influence of bending cycles on the sensor performance, we performed dynamic H₂ response measurements up to 5 kPa using a test system of our own design (Figure 3a) before and after 500 bending cycles. First, we surveyed the effects of bending cycles on the baseline...
current (at 1 V bias). A Pd NP film with an initial current of 21.41 nA was built upon a 0.25 mm-thick PET sheet by performing deposition of Pd nanoclusters at a deposition rate of 0.2 ± 0.05 Å/s for 5 min. Analyzing from the TEM image of the TEM sample prepared under the same fabricating conditions, as shown in Figure S6 in the Supporting Information, the thickness and roughness of this Pd NP film are 2.1 and 5.3 nm, respectively. Electrical current of the Pd NP film was measured during 500 bending cycles and compared to the baseline current before starting the test. The strain ε induced by the bending can be expressed as ε = T_s/2R_b, where T_s is the substrate thickness and R_b is the radius of curvature of the sample. The maximum strain is about 1.47% when the sample was bent at the maximum degree of bending, corresponding to minimum radius of curvature 8.5 mm (the inset in Figure 3b). Here, we performed this test at device bending orientations with respect to the microelectrode orientation: perpendicular and parallel to the fingers of the IDE (Supporting Information, Figure S7).

Figure 3b shows the relative baseline current change (ΔI_0/I_0) as a function of bending cycles, where I_0 is baseline current of the sample (the error bars of the plots at parallel bending orientation are too small to be distinguished in Figure 3b). First, the device was tested at perpendicular bending orientation. Notably, a gradually increasing trend of ΔI_0/I_0 was observed during the first 120 bending cycles, and then the ΔI_0/I_0 remained stable at about 5.9%. As a result, the baseline current increased from approximately 21.41 to 22.68 nA. The microscopic mechanism causing the baseline current variation in the bending cycles may be due to a few NPs’ rearrangement, resulting in the change in electrical conductivity. The bending cycle test at parallel bending orientation was also performed and the result indicated a negligible decrease in baseline current which is much less than that at perpendicular orientation. Such a large difference in baseline current change between perpendicular and parallel bending orientations may be attributed to the anisotropic rearrangement of NPs.

The sample was characterized by SEM before and after the bending cycle test. We compared the morphology of the NP film before and after the bending cycle test, as shown in Figure S8. These two SEM images were taken from two different regions of the sample as it is hard to focus the field of view on the same area of the sample before and after the bending cycle test. However, we can see in Figure S8 that there is not much difference between the overall morphology of the Pd NP film on the PET sheet before and after the bending cycle test. The maintaining of the film morphology after bending cycles can be attributed to the discrete-grain structure of the film as well as...
the strong adhesive force between the NPs and the substrate. The strong adhesive force stems partly from high flying speed of the nanoclusters during the deposition process. The stability and robustness of the film morphology makes it possible for this nanostructure to act as a flexible sensing device. Siffalovic et al. showed that an NP monolayer was preserved on a stretched Mylar membrane strained up to 11% and that no disintegration into separate islands took place. Referring to this result, we surmise that the undisturbed baseline current following the upward trend enables the sensor to run stably and reliably without performance degradation, although a slight baseline drift was observed in the initial stage of the bending cycle test process. To confirm this, we compared the H₂-sensing response before and after the bending cycles. Figure 3c–e compares the H₂-sensing response of the Pd NP film before and after the bending– unbending recycle test. The relative change in the current signal \( \Delta I/I_0 \) is \( (I - I_0)/I_0 \) \times 100% is defined as the sensing response amplitude, where \( I \) is the current of the sensor exposed to the target gas. Overall, the device exhibited a very similar H₂-sensing response before and after the bending– unbending cycle test, as shown in Figure 3d,e. The current of the sensor increased in the presence of H₂, indicating that the H₂-sensing mechanism of the Pd NP film was not changed by the bending cycles and remained based on HILE. Further, there was a negligible deviation between the calibration curves of the H₂ sensor before and after the bending– unbending cycle test, as demonstrated in Figure 3c, which indicates that the sensor is able to withstand repeated mechanical deformation without significant degradation in the H₂-sensing performance. The calibration curves, similar to the results of our previous studies, exhibit three discrete response regimes with different slopes corresponding to three phase regions of Pd hydride, i.e., the α phase region, the α—β phase coexistence region, and the β phase region, which further confirms that the bending cycles had no effect on the H₂-sensing mechanism with respect to the Pd NP film and flexible polymer combination. The stable H₂-sensing behavior can be attributed to the discontinuous structure of the Pd NP monolayer, in which the discrete NPs shift with increasing substrate stress and are preserved on the strained polymeric membrane rather than induce cracks as in continuous-metal layers or bulk metals. Repeated deformations have no irreversible effects on the surface morphology of the Pd NP film because of the discrete nanogranular structure. These results reveal that our H₂ sensor not only possesses prominent mechanical robustness and flexibility but also exhibits stable and reproducible H₂-sensing performance even after hundreds of bending cycles.

**Effect of Strain on the H₂-Sensing Behaviors.** Essentially, the electro-mechanical responsiveness of the flexible device derives from the interparticle electronic coupling that plays a key role in the charge transport properties of the metallic NP assemblies. On the basis of the fact that the interparticle electron coupling strength can be significantly altered by adjusting the interparticle separation, it seems reasonable to expect that the strains applied to substrates have a marked influence on the H₂-sensing behavior because of the potential strong correlation between the H₂-sensing mechanism and tunneling process.

To evaluate the effect of bending-induced strain on the H₂-sensing performance, the response to H₂ of the strained device, which was attached to the cylinder wall as depicted in Figure.
4a, was measured. Ignoring the thickness of the substrate and cylinder wall, the radius of curvature is 50 mm, half of the diameter of the cylinder, which resulted in about 5% tensile or compressive strains. The calibration plots for the device in the bent and flat states are compared in Figure 4b. The response characteristics of the device in the bent states are overall quite similar to that in the flat state. Sigmoidal calibration curves were observed for all bent and flat states of the sensor, but, ignoring this basic similarity, differences in the response amplitude, and slopes of the calibration curves were also observed. Here, we are more concerned with the sensing behaviors at low range of hydrogen pressures because there is a nonnegligible need for accurate detection of H2 at low concentrations. This result reveals that our sensor is able to respond at H2 pressures of 500 Pa, respectively, indicating that the sensitivity of the H2 sensor was enhanced by up to 64%, compared with that in the unstrained situation, by applying a tensile strain. The slope of the calibration curve and the response amplitude (ΔI/I0) for tensile strain was larger than that of the flat state, whereas the slope of the sensor calibration curve and the response amplitude for compressive strain was smaller than that in the flat state, which suggests that the tensile and compressive strain had a positive and negative influence, respectively, on the sensitivity of the H2 sensor.

In view of the HILE-based H2-sensing mechanism, the sensitivity depends on lattice expansion induced changes in the cotunneling current and the initial current flowing through the percolation network in the Pd NP film. For concave bending of the device, the I0 increases with increasing compressive strain because of the shorter interparticle distance. Additionally, the change in the I caused by the lattice expansion will decrease because the interparticle space is squeezed by the compressive strain, limiting swelling of the Pd NPs. Consequently, under the effects of decreased variation in the response current and the incremental increase in the initial current induced by compressive strain, the sensitivity will clearly be reduced. In contrast, the tensile strain provides more freedom for the NPs to swell in space, by loosening the NP percolation network and also reducing the I0, resulting in a higher overall sensitivity than that in the flat state.

In the case of the β phase region, a monotonic correlation of the response amplitude with H2 pressure at the same slope value of 0.0031 ± 0.0002% Pa−1 and no saturation response was observed up to 10 kPa (Figure S10), indicating that the device is capable of quantitatively detecting H2 in this high hydrogen pressure range which corresponds to 10% hydrogen concentration. This result reveals that our sensor is able to respond to H2 with the dynamic response range as wide as 0–10%.

Furthermore, the device under 5% tensile strain was tested to various pressures of H2 in the α phase region at RT (∼22 °C), 35 and 50 °C to assess the effect of temperature on sensing properties due to the time- and temperature-dependent viscoelastic nature of the PET substrate. The experimental setup was the same as for the tests in Figure 3a, except that a ceramic heating cylinder with 25 mm diameter, controlled by a proportion–integral–derivative controller, was used to provide different ambient temperatures and a known deformation, ε = 1%, as shown in Figure S11a. The raw data of the response signal at various temperatures can be found in Figure S11b–d. In general, the H2 sensor exhibited positive response (ΔI > 0) under all the test temperatures. The response amplitude versus H2 pressures graph of the bent device exposed to H2 at indicated test temperatures was plotted in Figure 4d. The response amplitude and sensitivity of the bent device decreased concomitantly with the increasing temperature. This can be mainly attributed to the reduced solubility of H in PdH1. On the basis of the natural absorption behavior of Pd materials with H2 molecules, it is reasonable to propose that, at higher temperatures, a lower solubility of H atoms in PdH may produce smaller changes in the crystal grain volume during gas absorption, thus reducing the response amplitude of the NP film to H2.

However, the reduction in response amplitude was much smaller at 35 °C compared to that at 55 °C. Thanks to the negligible degradation in response amplitude at 35 °C, which is close to human body temperature, our sensors showed potential application prospects in wearable devices.

We now investigate the performance of the H2 sensor with respect to response time. The response of the flexible sensor to a series of rapid H2 loadings was measured to evaluate its kinetic characteristics in different strain states. To test this, the sample was sealed inside a small cell that was connected to the test chamber through a high-speed electromagnetic valve, as shown in Figure S12 in the Supporting Information. The response time is defined as the time required for the increase in the current ΔI to reach 0.9ΔI max (where ΔI max is the maximum change in the response current for H2 loading) after the sensor is exposed to a given H2 pressure. The normalized response signal ΔI/ΔI max versus time plots for the device in the strain and flat states are shown in Figure 5a. It is evident that the change in current of the sample initially increased with time and then saturated at a value that depended on the H2 pressure. Fast response times of 4.62 and 2.74 s were measured at H2 pressures of 500 ± 25 and 10 000 ± 500 Pa, respectively, in the flat state. It is worthy of noting that the detector response time not only depended on the H2 pressure but was also greatly affected by the applied strain. As the sensor was bent at tensile strain, the response time diminished, with values of 3.44 and 1.41 s at H2 pressures of 500 ± 25 and 10 000 ± 500 Pa, respectively, whereas in the case of compressive strain the response time was prolonged to 9.36 and 7.6 s, respectively.

To further investigate the sensing kinetic characteristics of our flexible H2 sensor, the comprehensive trends of the response time as functions of H2 pressure in the flat and bent states are shown in Figure 5b. As might be expected, the response time in all strained states is noticeably shortened with increasing H2 pressure, except for a slow-response peak because of the large lattice expansion caused by nucleation and growth of the β phase in the α matrix, similar to the
Device sensing kinetics under strain. (a) Normalized response curves at H2 pressures of 500 ± 25 and 10 000 ± 500 Pa in the flat, tensile strain, and compressive strain states. The horizontal dashed lines indicate ΔI/ΔI_{max} = 0.90. (b) Response time vs hydrogen pressure plots for the sensor in the flat, tensile strain, and compressive strain states on a linear-log scale. The inset shows the schematic illustration of the effect of strain on the diffusion length. The dashed lines denote the diffusion paths of hydrogen atoms in the Pd NPs.

Figure 5. Device sensing kinetics under strain. (a) Normalized response curves at H2 pressures of 500 ± 25 and 10 000 ± 500 Pa in the flat, tensile strain, and compressive strain states. The horizontal dashed lines indicate ΔI/ΔI_{max} = 0.90. (b) Response time vs hydrogen pressure plots for the sensor in the flat, tensile strain, and compressive strain states on a linear-log scale. The inset shows the schematic illustration of the effect of strain on the diffusion length. The dashed lines denote the diffusion paths of hydrogen atoms in the Pd NPs.

More importantly, the device exhibited significant prolonging of the response time with compressive strain, while the reverse was observed for tensile strain. We attribute this phenomenon to the effects of strain on the diffusion path (the inset in Figure 5b) and release of stress on the interface between the flexible substrate and Pd NPs. When the device was subjected to tensile strain, the interparticle distance increased and created more space as well as adsorption sites, especially among neighboring NPs in the NP aggregation areas. An in situ small angle X-ray scattering study of the NP displacement was carried out and confirmed that the interparticle distance increased with loading tensile strain. Because of this, the diffusion paths of hydrogen atoms in Pd NPs were shorter (the inset in Figure 5b), resulting in considerable improvement in the response speed. On the other hand, a greater impact of compressive strain on the response time was observed (Figure 5b). Compressive strain hindered the sensing process by not only diminishing H2 reaction sites and extending the diffusion distance but also suppressing stress relaxation at the interface between Pd NPs and the PET substrate. In fact, H2 uptake in metallic Pd can result in compressive stresses in the gigapascal range. Additional compressive stress originating from the concave bending of the PET substrate will significantly prolong stress relaxation at the interface between Pd NPs and the PET substrate, leading to slowing of the response time. Collectively, affected by the extension of the diffusion distance and the additional stress relaxation, the response time was more sensitive to compressive strain than to tensile strain. These experimental results unambiguously show that a flexible H2 sensor with a sub-10 s response time has been achieved. It is possible, but unconfirmed, that the flexible polymeric substrate with a low elastic modulus is mainly responsible for the fast response, due to the relatively mild stress relaxation.

Limit of Detection for Hydrogen Gas. Now, we turn to the limit of detection for H2 (LOD_{H2}). The response to a low-concentration (130—760 ppm) H2/Ar mixture was investigated (Figure 6). The sensor exhibited a significant response to a 130 ppm concentration of H2 with about 0.487% change in the response amplitude, which is much higher than the electronic noise. This indicates that the LOD_{H2} of the sensor is less than 130 ppm. To obtain a reliable LOD_{H2}, we determined its value from the experimental data and by calculation using the signal-to-noise method. In the case of the response to 130 ppm H2, the signal-to-noise ratio (SNR) was about 8.85 (the inset in Figure 6). The detection limit can thus be conservatively estimated as LOD_{H2} = 130 ppm/SNR ≈ 15 ppm. This value is low enough for H2 leak detection, because the lower explosion limit for H2 is 4%.

Response to H2/Air Mixture in Different Humidity Environment. Finally, the influence of RH on the sensing behaviors was investigated for its importance in developing sensors operable in the atmospheric environment. Figure 7 shows the response to H2 in air with concentrations of 1, 0.6, and 0.3 mL measured at various humidity levels from 0 to 90% at RT. The response signals, in which current growth curves upon H2 exposure were observed in Figure 7a, are similar to the responses to pure H2. This illustrates that the water vapor present in the humid air should not have effect on the sensing mechanism during the hydriding and dehydriding of Pd NPs. However, the response amplitude (ΔI/I_0) of the flexible H2 sensor decreased with the RH increased at the testing concentrations of H2. Up to 90% RH, the response and recovery speed became significantly slower. This result was reasonable because the physisorbed water vapor occupied the active sites of the Pd NPs, weakening the ability of the surface to adsorb H2 molecules, and thus slowing the device sensing kinetics. However, overall, our sensors can be operated in the RH range of 0—90%.

Comparison of Different Nanomaterial-Based H2 Sensors. We compared the key metrics of our sensor with recently developed nanomaterial-based H2 sensors, as

Figure 6. Real time response to the H2/Ar mixture. The concentration (in ppm) for each hydrogen loading is marked at the top of each response peak. The inset shows the magnified image of the response peak for 130 ppm H2, from which the signal-to-noise ratio (SNR = H/h = 8.85) is extracted.
strain on the H2-sensing behaviors was investigated. In the response to H2/air mixture with concentrations of 1, 0.6, and 0.3% in degradation after 500 bending cycles, showing good 

1). Furthermore, the coupling of Pd NP unique interparticle electrical responsiveness. The e
sensors, to the best of our knowledge (see Table | ACS Applied Materials & Interfaces | Research Article | DOI: 10.1021/acsami.8b15445

summarized in Table 1.18,19,41,46—51 Although the H2-sensing performance of our sensor is predominantly influenced by the applied strain, its overall performance is better than other sensors, to the best of our knowledge (see Table 1). Furthermore, the coupling of Pd NP film assemblies and flexible substrates reduces cost and complexity of the devices.

| CONCLUSIONS |

We have realized an optically transparent and flexible HILE-based H2 sensor by depositing a Pd NP film onto a PET substrate. The H2 responsiveness showed no performance degradation after 500 bending cycles, showing good flexibility, robust electromechanical properties, and stable H2-sensing behavior because of its discrete nanogranular structure and unique interparticle electrical responsiveness. The effect of strain on the H2-sensing behaviors was investigated. In the α phase region, a linear dependence between the response amplitude ΔI/I0 and P2H1/2 was observed. The influence of tensile and compressive strains under bent state on the H2-sensing performance was systematically evaluated. A tensile strain was found to produce greater sensitivity, which was enhanced by up to ~64% compared with the unstrained situation, owing to more freedom to swell in space and the lower initial current baseline induced by tensile strain. Moreover, the loading of tensile and compressive strain produced a positive and negative influence, respectively, on the sensing kinetics of the flexible H2 sensor. The ability to detect a H2 concentration as low as 15 ppm, a dynamic response range as wide as 0~10% and sub-10 s response time were achieved. In addition, the flexible transparent sensor can be operated in the RH range of 0~90%. Compared with other conventional rigid-substrate-based H2 sensors, our sensor can be fabricated using a controllable low-cost process, and also displays superior sensing performance. The nanogranular film described in this work holds promise for the development of flexible, transparent, and wearable sensors for chemical detection in the coming era of the Internet of Things.

| Table 1. Sensing Performance for Nanomaterial-Based Resistive H2 Sensors |
|------------------|------------------|------------------|------------------|------------------|
| sensing element  | response amplitude (%) | detecting range (ppm) | LODH2 (ppm) | response time (s) | flexibility |
| single Pd NW46   | 3 (0.1%)          | 2 ppm—10 ppm      | 2              | ~400 (0.1%)     | no          |
| CNT network49    | 1000 (311 ppm)   | 0.89—311 ppm      | 0.89           | 7 (311 ppm)     | no          |
| Pd NPs@Si nanomesh50 | 10 (0.1%)       | 50 ppm—0.8%     | 50             | 12 (0.1%)      | no          |
| Pd NPs/graphene  | 54.1 (2%)        | 0.2—2%           | 2000           | 6 (2%)         | no          |
| Pd/Mg NWs mesh 19 | ~11.7 (10 000 ppm) | 10—40 000 ppm   | 10             | ~6 (10 000 ppm) | yes         |
| Pd NWs@ZIF-8 41  | 0.3 (0.1%)       | 1000 ppm—1%     | 1000          | 13 (0.1%)      | no          |
| Pd@Ag HNWs18     | 0.89 (900 ppm)   | 100—900 ppm      | 100            | 120            | yes         |
| Pd—PMMA hybrid film47 | ~100 (2%)       | 600 ppm—10%     | 600            | ~0.38 (2%)     | yes         |
| network of Pd/Cr NWs 41 | ~4 (0.1%)     | 0.1—100%         | 1000          | ~27 (0.1%)     | no          |
| Pd NP film (this work) | ~5.5 (0.1%)6    | 15 ppm—10%      | 15             | ~6 (1000 ppm)  | yes         |

Abbreviations: CNT = carbon nanotube; HNW = hollow nanowire; NP = nanoparticle; NW = nanowire. *Pure H2 pressures were converted to hydrogen concentrations by assuming a 1 atm ambient pressure. The key metrics of our sensor were extracted from the experimental data in the flat state. The detecting range is the gas concentration measured in the study. It may not exactly reflect the actual limited working range for the sensors.
the PET substrate, and the Pd NPs were deposited onto it simultaneously. The microstructure of the Pd NPs was characterized using a STEM (JEOL, JEM2100F). The image was acquired in the HAADF-STEM mode. For further analysis of the surface topography of the Pd NP films, we performed transmission electron microscope (TEM, FEI Tecnai F20s Twin) at low magnifications. The surface of the Pd NP films on the flexible PET substrate was characterized using a field emission scanning electron microscope (FE-SEM, Hitachi, SU8010). Optical characterization was carried out using an ultraviolet–visible–near-IR spectrophotometer (Agilent, Cary 5000) in the wavelength range of 400–1500 nm. Experimental details of the measurement of spectral transmittance are provided in Figure S5 in the Supporting Information.

**Electromechanical Properties Measurement.** In the bending cycle test, the sensor, clamped by two programmable stepper-motor-controlled sliders (see the inset in Figure 3b), was subjected to bending–unbending cycles in which the two sliders moved back and forth. The current (at 1 V bias) of the flexible sensor in the bent and flat states was measured by the sourcemeter (Keithley 2636B).

**Gas-Sensing Measurement.** As shown in Figure 3a, characterization of the pure H2-sensing behavior of our devices was carried out in a test chamber of our laboratory, which was connected to a mechanical pump by a valve and could be evacuated in the H2 loading and unloading cycles. Pure H2 or an H2/Ar mixture (the test gas) was introduced to the test chamber at a constant gas flow rate of 200 sccm using a mass flow controller (Sevenstar, D07-7A/ZM). The pressure of pure H2 (P0) in the test chamber was monitored by a piezoresistive gauge (Zhenghua, ZJ-1P) because the sensor responds, in principle, only to H2 partial pressure. H2/Ar mixtures with different concentrations were obtained by adjusting the H2 and Ar gas flow with the help of high-precision mass flow controllers. The sensor was connected to the sourcemeter (Keithley 2636B) by an electrical feedthrough, to measure the current (at bias voltage of 1.0 V) during H2 sensing. In order to measure the H2-sensing properties under strain, the flexible device was bent by wrapping it around the external (convex bending) and internal (concave bending) surfaces of a cylinder, as shown in Figure 4a.

The schematic diagram of the measurement configuration used for response time measurements is showed in Figure S12. The tested samples were sealed inside a small cell (~100 mL) which was connected to the intrinsic testing chamber (~30 L) through a highspeed electromagnetic valve. The large chamber was filled with H2 to a predetermined pressure, and then a rapid H2 loading was switched into the small cell as the electromagnetic valve was rapidly opened. Because the small cell’s volume is far smaller than that of the large chamber, the H2 pressure changes are negligible during the formation of the H2 loading.

For measuring the LODH2 of the sensor, a gas mixer was equipped between the test chamber and mass flow controllers in order to obtain low concentration H2, as shown in Figure S13. During the tests, 300 sccm Ar gas, controlled using a mass flow controller, was continually flowed through the gas mixer into the chamber, and the H2/Ar mixture of 1% concentration was also flowed through the gas mixer into the chamber in the form of pulse at a different flow rate. The concentration of H2 can be obtained from the flow ratio of the two gases.

The setup for H2 sensing in different humidity environment is schematically shown in Figure S14. By bubbling dry air in water and changing the flow rates through the mass flow controllers, the humidity of the target gas is controlled. The mixture of dry, wet, and hydrogen-containing air flowed through the test chamber with the flow rate of 1000 sccm. A hygrometer was placed nearby the sample to obtain the ambient humidity.

**ASSOCIATED CONTENT**

1. Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b15445.

Evaluation of the current between the IDEs during Pd NPs deposition; HRSTEM image of neighboring NPs; TEM images of the same Pd NP film characterized by STEM in Figure 2 at randomly selected 8 regions; spectral transmittance of the Pd NP films on PET sheets for different deposition times from visible to near infrared wavelength region; schematic diagram of the transmission measurement; the analysis of the thickness and roughness of this Pd NP film; illustrations of the device bending orientations in the bending cycle test; theoretical analysis of the calibration curve; plots of the data from Figure 4b in the β phase region on a linear scale; schematic diagram of the measurement configuration used for gas-sensing measurement (Figures S11–S14) (PDF)

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**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China (grant numbers 51871091, 11627806, 21802038, 11604161, and 11604310), the Scientific Research Project of Education Department of Hubei Province (grant number Q20182505), the Hubei Key Laboratory of Pollutant Analysis and Reuse Technique (Hubei Normal University) (grant number PA20170204), the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (grant number 16KJB140009), and the Natural Science Foundation of Jiangsu Province (grant number BK20160914).

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