Extremely Deformable, Transparent, and High-Performance Gas Sensor Based on Ionic Conductive Hydrogel

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ABSTRACT: Fabrication of stretchable chemical sensors becomes increasingly attractive for emerging wearable applications in environmental monitoring and health care. Here, for the first time, chemically derived ionic conductive polyacrylamide/carrageenan double-network (DN) hydrogels are exploited to fabricate ultrastretchable and transparent NO2 and NH3 sensors with high sensitivity (78.5 ppm−1) and low theoretical limit of detection (1.2 ppb) in NO2 detection. The hydrogels can withstand various rigorous mechanical deformations, including up to 1200% strain, large-range flexion, and twist. The drastic mechanical deformations do not degrade the gas-sensing performance. A facile solvent replacement strategy is devised to partially replace water with glycerol (Gly) molecules in the solvent of hydrogel, generating the water−Gly binary hydrogel with 1.68 times boosted sensitivity to NO2 and significantly enhanced stability. The DN-Gly NO2 sensor can maintain its sensitivity for as long as 9 months. The high sensitivity is attributed to the abundant oxygenated functional groups in the well-designed polymer chains and solvent. A gas-blocking mechanism is proposed to understand the positive resistance shift of the gas sensors. This work sheds light on utilizing ionic conductive hydrogels as novel channel materials to design highly deformable and sensitive gas sensors.

KEYWORDS: gas sensor, stretchable, double-network hydrogel, transparent, water retention

1. INTRODUCTION

Flexible and stretchable electronic sensors have attracted considerable interest in the past decade because of their emerging applications in health assessment, internet-of-things, electronic skin (e-skin), robotics, and environmental monitoring.1 Among various applications, gas sensing has become increasingly important because air pollutants, including carbon oxides (COx), nitrogen oxides (NOx), sulfur dioxide (SO2), ammonia (NH3), and so forth, have endangered both the environment and the health of humans.2 For example, the human respiration system may be damaged by nitrogen dioxide (NO2) with the concentration higher than 1 ppm.3 NO2 also participates in many processes of forming hazardous acid rain, ozone (O3), and photochemical smog.4 As such, US Environmental Protection Agency (EPA) set a 1 h and the annual average NO2 standard of 100 and 53 ppb, respectively.5 Otherwise, NO2 is very useful in the synthesis of nitric acid, which is an important chemical in the production of fertilizers for agriculture and explosives for military application.6 In addition, NO2, an important gut neurotransmitter, also plays a significant role in regulating mucosal blood flow, intestinal motility, and secretory functions.7,8 NO2 can be used as a biomarker in the noninvasive detection of diseases such as lung infections and bowel disease.9 NH3 is a toxic and colorless gas that may cause respiratory tract irritation at low concentration from 50 to 100 ppm.9,10 It can also be utilized as a biomarker for disease diagnosis.9 Hence, development of gas sensors that can precisely detect NO2 and NH3 at low concentrations can protect people from being harmed by these toxic gases and improve the accuracy of diagnosing the diseases closely related to the levels of these gaseous chemicals. Especially, if these gas sensors can work at a flexible/
stretchable state, they can be used for emerging wearable applications in health care and environmental safety. For instance, the flexible/stretchable gas sensors can be conformably attached on curved surfaces, such as clothes, bags, animals, and plants, for real-time gas monitoring.

Existing flexible gas sensors are fabricated by integrating inorganic gas-sensitive materials including graphene, MoS\(_2\), carbon nanotubes, colloidal quantum dots (CQDs), and so forth on flexible substrates. However, this structural engineering method demands additional flexible substrates and fabrication procedures. Furthermore, applications such as e-skin, soft robotics, and wearable devices require the sensors to sustain larger mechanical deformation beyond bending, for example, stretching and twist. There are few reports on stretchable gas sensors fabricated by depositing graphene-based materials on stretchable substrates, such as polycrystalline siliroxane (PDMS) and Ecoflex. For example, Lee and co-workers reported a stretchable NO\(_2\) sensor using reduced graphene oxide (rGO) that was assembled on polyurethane (PU) nanofibres. The nanohybrids are deposited on the stretchable PDMS substrate, realizing up to 50% strain. Besides, Ha and co-workers reported a micro-supercapacitor array derived graphene gas sensor on a deformable Ecoflex substrate. A maximal biaxial 40% strain and a uniaxial 50% strain are enabled. However, such a structural engineering approach requires complicated experimental procedures to fabricate the multilayer-sensing devices with very limited stretchability. For example, the largest tensile strain is only 50% for state-of-the-art stretchable gas sensors. In addition to stretchability, transparency is also an important attribute in e-skin, wearable circuitry, and flexible display applications. In skin electronics, the transparency of sensors is important for the improvements of aesthetics in daily usage and the security in military applications. Nevertheless, conventional gas-responsive materials, electrodes, and interconnects are usually opaque, which significantly decrease the transparency of fabricated devices. A simple but effective alternative to impart high stretchability and transparency to gas sensors is the development of the sensing material that intrinsically possesses these attributes. However, to the best of our knowledge, this material has seldom been reported.

Recently, ionic conductive hydrogels have attracted widespread applications in soft electronics because of the good stretchability, conductance, transparency, and biocompatibility of the material. Especially, double-network (DN) hydrogels that consisted of two kinds of interconnected polymer networks exhibit better mechanical robustness, stretchability, and chemical functionalities than their single-network counterparts. In the hydrogel, the hydrophilic polymer chains are dispersed in water. The polymer network and liquid phase endow solid-like mechanical properties and flexibility to the hydrogel, respectively. Meanwhile, the movement of ions in liquid media endows conductivity to the hydrogel. Recently, many studies on graphene-based gas sensors reveal that the oxygen-containing functional groups such as \(-\text{OH}, \text{SO}_3^-,\) and \(-\text{NH}_2\) on graphene play an important role in enhancing the adsorption of NO\(_2\) and NH\(_3\) molecules. Considering the vital role of oxygen-containing functional groups in improving the gas-sensing performance, herein, we employ chemically functionalized polyacrylamide (PAM)/carrageenan DN hydrogel that contains abundant oxygenated groups to fabricate extremely stretchable, transparent, and sensitive NO\(_2\) and NH\(_3\) gas sensors. Differing from a traditional electron-conductive gas-sensing material, the ionic conductive DN hydrogel provides remarkable advantages of extreme stretchability (up to 1200% strain), flexibility, and transparency. Therefore, additional structural engineering is bypassed when it is used to fabricate stretchable chemical sensors. In addition to high sensitivity, selectivity, and fast response, good stability is also an important prerequisite for the practical application of a gas sensor. However, water loss induced instability is an intrinsic problem of hydrogels. The water evaporation may degrade the stretchability, conductivity, and stability of hydrogel-based devices in the long term. In order to enhance the water retaining ability of hydrogels, herein, a facile solvent replacement method is proposed to introduce hygroscopic glycerol (Gly) in the solvent of DN hydrogel. The chemical modification of hydrogel with Gly molecules not only brings 1.68 times increased sensitivity in NO\(_2\) detection but also ensures the stability of the gas sensors for as long as 9 months.

2. EXPERIMENTAL SECTION

2.1. Materials and Synthesis of DN and DN-Gly Hydrogels.

All chemicals including acrylamide (AAm), \(\kappa\)-carrageenan, KCI, N-methylenebisacrylamide (MBA), and ammonium persulfate (AP) were purchased from Sigma-Aldrich. A one-pot polymerization method was used to synthesize the DN hydrogel with the total water content of 82% (wt %). The AAm and carrageenan with the weight ratio of 1:3 were dissolved in deionized water at 95 °C. Then, MBA with the weight percent of 0.05% relative to AAm and KCl with the weight percent of 6% relative to carrageenan were dissolved in the water pot and stirred magnetically at 95 °C for 5 h. Subsequently, AP with the weight percent of 0.5% relative to AAm was added and stirred for 1 min. The solution was gradually poured into a glass dish with the length, width, and height of 11, 11, and 2 cm, respectively. The system was stored at 5 °C for 1 h for the formation of carrageenan. Then, the system was heated at 95 °C for 1 h for the cross-linking of PAM. Finally, the synthesized DN hydrogel was cut into slices to investigate its properties.

For the preparation of DN-Gly hydrogel, the as-synthesized DN hydrogel was soaked in pure Gly for 20 min at room temperature. The weight of Gly in the container was 8 times more than that of DN hydrogel. The water in the DN hydrogel was partially replaced by surrounding plenty Gly in the soaking process. After the hydrogel was removed from the container, it was placed on a filter paper for 10 min to remove extra Gly on the surface.

2.2. Characterization.

The UV–vis spectra were acquired on a Shimadzu UV-2501PC. The Fourier transform infrared (FTIR) spectra were obtained on a PerkinElmer Frontier spectrometer. The tensile tests were implemented on an Instron machine (S6566) with the speed of 5 mm/min to obtain the stress-strain curves. The X-ray photoelectron spectroscopy (XPS) spectra were acquired on a PHI-5400 spectrometer (Physical Electronics, US) with an Al K\(_\alpha\) (1486.6 eV) X-ray source. Field emission scanning electron microscopy (SEM) (JSM 7600F, Japan) was deployed to characterize the morphology of hydrogel after freeze-drying.

2.3. Gas Sensing Measurement.

The gas-sensing test was carried out in a gas chamber with electrical feedthroughs. After applying a constant bias voltage of 1 V on the two electrodes of the chemiresistor, the resistance change of the sensor was monitored and recorded using a Keithley 2602 SourceMeter. In a typical sensing measurement cycle, synthetic air with 72% relative humidity (RH) was introduced into the chamber to clean it. Subsequently, test gas (NO\(_2\) or NH\(_3\)) balanced by synthetic air was introduced into the chamber for 300 s to record the response process. Finally, the synthetic air was injected into the chamber for 300 s to record the recovery process. All gas flows and the concentration of test gas were precisely controlled by mass-flow controllers. For all results, the sensor output was measured three times to obtain the average response value and the statistical error. For gas-sensing measurements at a stretched state, the hydrogel was stretched to a desired strain in
the first step; then two binder clips were used to fix the two ends of the hydrogel to an underlying glass slide; finally, the system was put in the chamber for gas-sensing test.

3. RESULTS AND DISCUSSION

The highly stretchable and transparent PAM/carrageenan DN hydrogel was synthesized via a one-pot sol–gel process, in which an ionic cross-linked carrageenan network and a covalently cross-linked PAM were formed in situ (Figure 1a). In the polymerization of PAM, MBA and AP were employed as a cross-linker and thermal initiator, respectively. All chemicals except AP were dissolved in a water pot and stirred magnetically at 95 °C for 5 h. Then, AP was added and stirred for 1 min. After the system was kept at 5 °C for 1 h, the first network of carrageenan formed. Subsequently, the system was heated at 95 °C for 1 h for the cross-linking of the second network of PAM. The thermal induced polymerization of PAM here differs from the previously reported photoinduced polymerization method.25,32 The DN-Gly hydrogel was prepared via a convenient solvent replacement process from the synthesized DN hydrogel. In brief, the as-synthesized DN hydrogel was soaked in pure Gly for the replacement of water molecules with Gly molecules. After 20 min, the water in the DN hydrogel was partially replaced by surrounding Gly due to the diffusion caused by concentration difference, leading to the formation of a water–Gly binary solvent. The hygroscopic Gly

Figure 1. (a) Schematic illustration of the synthesis of DN hydrogel via a one-pot polymerization method, followed by loading of Gly in hydrogel via a solvent replacement strategy. (b–d) Schematics showing that NO2 molecules can form hydrogen bonds with Gly, PAM, and carrageenan, respectively, which facilitate the adsorption of NO2 molecules on the hydrogel.
Figure 3. NO₂ sensing behaviors of the DN hydrogel sensor. (a) Dynamic response of the sensor to NO₂ gas with decreased concentration from 1 to 0.1 ppm. The white and shaded regions denoted "off" and "on" states of a test gas, respectively, in the chamber. (b) Quantitative response variation vs NO₂ concentration. (c) Dynamic response of this sensor to NO₂ with the low concentration of 100 ppb. (d) Relative resistance change vs experimental cycle. (f) Investigation of the response time and recovery time in the detection of 500 ppb NO₂.

not only effectively inhibits the evaporation of water in the hydrogel (water retention) but also facilitates the adsorption of NO₂ and NH₃ molecules on the hydrogel by forming hydrogen bonds with them (Figure 1b). In addition to the –OH on Gly, –NH₂ on the polymer chain of PAM together with –OH and SO₃⁻ on carrageenan can also promote the adsorption of NO₂ and NH₃ molecules by forming hydrogen bonds with these gas molecules, leading to an increased sensitivity in gas detection (Figure 1c,d).

The transmittance spectra of DN and DN-Gly hydrogels indicate that both of them are highly transparent (>75% transmittance for ≥600 nm wavelength) (Figure 2a). The excellent transparency of the hydrogels is advantageous for wearable applications that require visualization.22,23 The O–H stretching peak at 3438 cm⁻¹ and O–H bending peak at 1651 cm⁻¹ appeared in the FTIR spectra of both DN and DN-Gly hydrogels (Figure 2b). Note that the DN-Gly hydrogel exhibited higher intensity in both the O–H stretching peak and the O–H bending peak in comparison with the unmodified DN hydrogel, suggesting that Gly molecules were successfully modified on the DN hydrogel. After solvent replacement treatment, the DN-Gly hydrogel did not show deteriorated stretchability, but displayed much higher mechanical strength compared with the unmodified DN hydrogel (Figure 2c). Specifically, the elastic moduli of DN and DN-Gly hydrogels within the linear range (0–70% strain) were calculated to be 299 and 502 kPa, respectively. Note that the elastic modulus of DN-Gly hydrogel is also much higher than that of carrageenan (72 kPa), PAM single-network hydrogels (9 kPa), and many other PAM-based DN networks, demonstrating the enhanced mechanical toughness.23,32,41 The high elastic modulus of DN-Gly hydrogel may be attributed to the formation of hydrogen bonds between Gly and PAM, as well as that between Gly and carrageenan.23 The hysteresis loop appeared in the loading–unloading curves is ascribed to the energy dissipation in the stretching process.42 XPS elemental analysis demonstrates that the DN hydrogel has a high content of C (78.13%), small amounts of O (16.03%), some N (5.11%), and little S (0.74%) (Table S1). Although the contents of K and Cl were too low to be detected in the quantitative XPS elemental analysis, they could be discerned in the XPS elemental spectra (Figure 2d–f). The SEM images show that enormous microscale pores appear on the freeze-dried DN hydrogel (Figure S2). The porous system plays an important role in facilitating gas adsorption by allowing gas molecules to diffuse into the abundant pores.

Both DN and DN-Gly hydrogels can withstand large and rigorous mechanical deformations, including stretching strain, bending, and twist, without breaking their structures (Figures 2g–i and S3–S5). For instance, the DN-Gly hydrogel remained intact when it was twisted 540°, bent 120°, and stretched up to 1200% strain, which is the highest value for reported gas-sensing materials so far.21 Detailed photographs of the two kinds of sensors at different strains are shown in Figures S3 and S4. The DN-Gly hydrogel remained conductive even when large deformations were applied, including 40% strain, 180° twist, and 120° flexion (Figure S5d–f). The excellent stretchability of DN and DN-Gly hydrogels is attributed to the efficient energy dissipation by unfolding the PAM chain and dissociating the double helices of carrageenan in the stretching process. Furthermore, the PAM network and carrageenan can interact with each other by forming hydrogen bonds.29,32 The synergistic effect between the binary networks could also dissipate energy.21 In addition, Gly molecules can form hydrogen bonds with both PAM and carrageenan, further enhancing the mechanical stretchability and toughness of the DN-Gly hydrogel.23 Investigation of the electromechanical property of the DN hydrogel revealed that the resistance of DN hydrogel nearly did not change with various angles but increased linearly with tensile strain from 0 to 133% (Figure S6).

The water loss induced long-term instability is an intrinsic problem of hydrogels.33,40 The loss of water makes hydrogels both rigid and nonconductive in the long term, which may seriously impair the performance of fabricated electronic devices and thus hinder their practical applications. The DN hydrogel had the weight loss as high as 74% when it was exposed to ambient air for 72 h (Figure 2k), whereas the weight loss decreased to as low as 28% after the hygroscopic Gly was introduced in the DN-Gly hydrogel. Furthermore, the
DN-Gly hydrogel was still conductive when it was exposed to ambient air for 72 h without encapsulation, demonstrating the significantly improved water retention capability and stability. In addition, the DN-Gly hydrogel did not shrink and harden when exposed to 55% RH at 40 °C for 50 h and could still withstand large mechanical deformations, including 360° twist and 120° flexion without breaking or fracture (Figure S7).

The gas-sensing performance of the DN hydrogel is evaluated by monitoring its relative resistance variation (ΔR/R₀) upon exposure to a test gas. Both the test gas exposure time and air purging time were 300 s. The quantitative response here is defined as the relative normalized resistance difference between ΔR/R₀ at the beginning of test gas “on” and that at the end of test gas “on” for each experimental cycle. Figure 3a displays typical dynamic response curves when the DN hydrogel sensor was exposed to NO₂ gas with a range of different concentrations (1–0.1 ppm). The sensor exhibited an immediate resistance increase upon exposure to NO₂. The positive resistance variation implied that the movement of ions (K⁺ and Cl⁻) in the hydrogel was hampered by the NO₂ gas molecules dissolved in the hydrogel. The response decreased monotonically with reduced NO₂ concentration in the reversible sensing (Figure S8). With decreased NO₂ concentration, fewer NO₂ molecules dissolved in the hydrogel and therefore the occurrence of blocking effects was smaller. It was worth noting that a remarkable linear relationship was observed between response and NO₂ concentration, which is desirable in practical application (Figure 3b). This DN hydrogel demonstrated its capability to detect NO₂ with the low concentration of 100 ppb (Figure 3c). When the DN sensor was exposed to 500 ppb NO₂ repeatedly in three consecutive experimental cycles, a nearly constant response of 18.2% with a small variation of 0.5% was observed, demonstrating the good repeatability (Figure 3d,e). The response time t₅₀ and recovery time t₉₀ are defined as the time required for a 50% signal change in the full magnitude of response factor in a sensing cycle. Analysis of the detection of 500 ppb NO₂ in one cycle reveals the response and recovery time of 10.1 and 46.8 s, respectively (Figure 3f).

One distinct advantage of the DN hydrogel based NO₂ sensor is its ability to work under various mechanical deformations, which do not adversely affect the sensitivity of gas detection (Figure 4a–d). Specifically, no obvious degraded response to 1 ppm NO₂ was observed when the DN sensor was twisted 180°, bent 180°, and stretched to 100% strain. In contrast, the response increased from 35% to 82.5% with increased strain from 0 to 100% (Figure 4c). The boosted response with strain may be resulted from the increased interaction surface area between gas molecules and hydrogel upon stretching. This assumption is further supported by the immunity of this sensor to twist and flexion, which have little effect on the surface area exposed to NO₂ gas. Furthermore, the unzipping of polymer chains and the alignment of ionic conduction paths in the stretching process may also increase the response. These hydrogel-based stretchable gas sensors with tunable sensitivity provide advantages over traditional rigid gas sensors that only exhibit fixed sensitivity once the sensors are made. In practical applications, the deformable gas-sensing system can be calibrated by integrating a strain sensor to preclude the influence of strain on gas sensing.

Importantly, chemical modification of DN hydrogel with Gly can significantly boost the sensitivity of NO₂ detection, as the hydroxyl groups on Gly molecules can form hydrogen bonds with NO₂ molecules, facilitating NO₂ adsorption. For example, the DN and DN-Gly sensors exhibited quantitative responses of 142 and 238%, respectively, to 5 ppm NO₂, an indication of 1.68 times increased response by chemical modification with Gly (Figure 4e,f). The enhancement in sensitivity was also evidenced by detecting NO₃ with other concentrations. In addition to sensitivity, the DN-Gly NO₂ sensor also showed higher recovery percentage compared with the DN sensor, demonstrating the feasibility of chemical modification in improving the comprehensive sensing performance (Figure S9). The limit of detection (LOD) of a chemical sensor can be determined when the signal level is 3 times higher than the noise level. Thereby, the theoretical LOD can be deduced by calculating the noise level (root-mean-square deviation) and
sensitivity (slope of linearly fitted response vs gas concentration curve) (Supporting Information). Along this line, the sensitivities of DN and DN-Gly sensors are calculated to be 33.2 and 78.5 ppm, respectively, and the LOD values of DN and DN-Gly sensors are calculated to be as low as 4.7 and 1.2 ppb, respectively (Figure S10 and Tables S2–S4). The exceptionally low LOD is attributed to the high sensitivity and the low noise level (0.05% for DN and 0.03% for DN-Gly), which may be related to the unique movement manner of charge carriers in the liquid phase. The LOD of this hydrogel sensor is not only much lower than the annual average NO2 exposure limit recommended by US EPA (53 ppb), but is also lower than that of most NO2 sensors based on other sensing materials (Table 1). For instance, the RGO/Cu2O composite, single-walled carbon nanotubes (SWCNTs), and PbS CQDs only display the LOD of 64, 44, and 84 ppb, respectively, in NO2 detection. Furthermore, the sensors based on these conventional materials are generally non-deformable and opaque. In addition, the sensitivity of our hydrogel-based sensor is also very competitive when compared with other high-performance NO2 sensors, including graphene-related, MoS2, and CNT-based NO2 sensors. It demonstrates the remarkable advantages of ionic conductive hydrogel in fabricating ultrasensitive and deformable NO2 sensors.

In addition to NO2, the DN hydrogel also shows appreciable response to NH3, a toxic and colorless gas with pungent odor (Figure 5). Similar to NO2 detection, the DN hydrogel also exhibited positive resistance variation upon exposure to NH3. This phenomenon reinforced the aforementioned mechanism that the gas molecules blocked ion movement upon adsorption and solvation. The DN hydrogel sensor was employed to detect NH3 in a wide concentration range (2–50 ppm). The response increased monotonically from 3.5% to 50.4% with increased NH3 concentration from 5 to 50 ppm (Figure 5a,b). A sensitivity of 1.3 ppm−1 was obtained by executing the linear fitting for the response versus NH3 concentration curves (Figure 5b). Notably, the sensor exhibited evident response to NH3 with the concentration as low as 2 ppm (Figure 5c). Although further diluted NH3 gas was not available for our current setup, careful analyses of the noise level and extrapolation of LOD reveal an exceptionally low theoretical LOD of 0.22 ppm NH3 (Figure S11 and Tables S5 and S6). Both the sensitivity and LOD displayed by this NH3 sensor are competitive in comparison with those of state-of-the-art NH3 sensors (Table S7). Similar to NO2, NH3 molecules can also interact with a large amount of oxygenated functional groups including –OH, SO3, and –NH2 in the hydrogel via hydrogen bonds, promoting their adsorption. Importantly, this hydrogel-based NH3 sensor provides unique merits of good stretchability and high transparency. Furthermore, the response of this sensor to 40 ppm NH3 slightly increased with strain (Figure 5d). From the dynamic response curves, the response and recovery time were derived to be as short as 22.5 and 13 s, respectively, which were competitive with many other NH3 sensors.

The sensing mechanism of the ionic conductive hydrogel is different from the conventional charge-transfer mechanism that is well known for carbon and semiconducting materials. For traditional metal oxides and graphene-based gas sensors, the resistance variation depends on both the electron-withdrawing/donating nature of analytes and the charge carrier type (electrons or holes) in the sensing materials. For example, the electron-withdrawing graphene with holes in the conduction band displays decreased and increased resistance upon exposure to oxidizing NO2 and reducing NH3, respectively. However, our hydrogel-based gas sensors exhibited a positive resistance variation regardless of the type of gas. It indicates that the blocking effect plays the key role in changing the resistance of hydrogel upon gas adsorption, which is similar to that of recently reported metallic Ti3C2T x MXene-based gas sensor. In the absence of NO2/NH3 gas, K+ and Cl− ions in the hydrogel could move freely, leading to a low resistance level (Figure 6a, left). When introduced, NO2/NH3 molecules diffused into the hydrogel and hindered the movements of ions, increasing the resistance (Figure 6a, right). The excellent sensitivity in NO2 and NH3 detection is attributed to the formation of hydrogen bonds between these gas molecules and a large number of oxygenated functional groups including –OH, SO3, and –NH2 on the polymer surface.
chains of PAM and carrageenan. The formation of hydrogen bonds promoted the adsorption of NO₂ and NH₃ on the hydrogels. The abundant −OH groups on Gly molecules further enhanced the sensitivity of DN-Gly sensor. In addition to hydrogen bond, other physical interactions such as van der Waals force also existed. These weak physical interactions led to a reversible sensing process. Upon adsorption, the gas molecules dissolved in water or Gly−water binary solvent. For NO₂ detection, some NO₂ molecules reacted with water, producing HNO₃ and NO. The unreacted NO₂ and newly generated NO molecules blocked the diffusion pathways of K⁺ and Cl⁻ ions, leading to the decreased charge carrier mobility and increased resistance of hydrogel. On the contrary, when the NO₂ concentration suddenly decreased in the atmosphere, the dissolved NO₂ and NO molecules left the hydrogel and diffused into the air because of the concentration difference. Because the blocking effect was removed, the resistance of hydrogel recovered. As oxygen is not involved in the NO₂ sensing process, this NO₂ sensor may also work in anaerobic environments. This is advantageous over traditional metal oxide chemiresistors, which must be operated in the presence of oxygen. For NH₃ detection, some NH₃ molecules may be oxidized to NO₂ molecules. The unreacted NH₃ molecules together with newly generated NO₂ molecules impeded the transport of ions in the hydrogel, leading to an elevated resistance level as well.

The selectivity of the gas sensors was investigated by exposing them to common interference gases, including 100 ppm CO₂, saturated ethanol, methanol, toluene, and acetone vapors and 72% RH (Figures 6b and S12). The magnitude of responses of this DN hydrogel sensor toward these interference gaseous chemicals was less than 7.5%, which was much smaller than that to NO₂ (100% for 2 ppm NO₂) and NH₃ (50.4% for 50 ppm NH₃), indicating the good selectivity. Because of the gas blocking effect, the sensor exhibited positive resistance variation toward all other measured gases except water. Water molecules could increase the volume of solvent upon adsorption and condensation and thus provide more space to facilitate the ion transport. Hence, the resistance of hydrogel shifted negatively when exposed to 72% RH (Figure S12f). The response of the DN hydrogel sensor to 72% RH (7.5%) is much smaller than that to 2 ppm NO₂ (100%), indicating the good selectivity relative to humidity. To further eliminate the influence of humidity, the DN-Gly hydrogel based gas sensor may be encapsulated by a porous and hydrophobic membrane in future work. This kind of membrane allows for selective passage of NO₂/NH₃ gas by blocking the passage of interference gaseous chemicals, like water. Thus, it is widely utilized in amperometric gas sensors.

The stability is vital for the life time and accuracy of a practical gas sensor. The water evaporation induced instability is a common concern for many hydrogel-based devices. Here, we exploited chemically modified DN-Gly hydrogel to improve the stability and thus prolong the life time of hydrogel-based sensors significantly (Figure 6c). Specifically, the DN hydrogel became nonconductive after 72 h and therefore could not be employed as a chemiresistor thereafter if without rehydration. Although rehydration of the DN hydrogel can restore its conductivity and gas-sensing ability in some degree, the gas-sensing performance degraded with prolonged time. In contrast, the DN-Gly sensor did not show appreciable degradation in its sensing performance even after 9 months. The remarkably improved stability of the DN-Gly sensor is attributed to the formation of hydrogen bonds between Gly and water molecules. Meanwhile, the enhanced sensitivity of DN-Gly to NO₂ is ascribed to the formation of hydrogen bonds between Gly and NO₂ molecules.
Various important intestinal gases including CO₂, H₂, and methane (CH₄) have been monitored by the ingestible sensor in situ and in real time to understand the functionality of the gut in the digestion process. However, NO₂, an important gut neurotransmitter, has yet to be monitored in situ. Attributing to the exceptional flexibility, biocompatibility, and high sensitivity, the ionic hydrogel-based gas sensors may be integrated in ingestible sensing capsules to monitor the intestinal NO₂ gas in future work.

4. CONCLUSIONS
In summary, we have successfully fabricated ultrastretchable gas sensors based on an ionic conductive DN hydrogel, which was found to be highly sensitive to NO₂ and NH₃ gases at room temperature. The DN-Gly hydrogel sensors exhibit high sensitivity (78.5 ppm⁻¹), selectivity, linearity, and exceptionally low theoretical LOD (1.2 ppb) in NO₂ detection. The excellent sensing properties are attributed to the interaction between gas molecules and enormous oxygenated functional groups covered on the hydrogel. The gas-sensing mechanism is dominated by the blocking effect brought by the dissolved gas molecules on the movement of conductive ions. This is different from conventional charge-transfer and electron depletion mechanisms that occurred on traditional gas-sensing materials. The room-temperature sensing operation brings low energy consumption and thermal safety. In addition to superior gas-sensing performance in comparison with previously reported gas-sensing materials, this ionic hydrogel provides unique advantages of extreme mechanical deformability and high transparency. For example, this hydrogel can be elongated up to 1200% strain, which is 24 times higher than previously reported gas-sensing materials. Furthermore, the mechanical deformations did not exert a negative effect on the gas-sensing performance. Note that the introduction of Gly molecules in the solvent of hydrogel via a facile solvent replacement strategy not only significantly enhanced the water retention ability and stability of gas sensors, but also boosted the NO₂ sensitivity 1.68 times. The response of the DN-Gly hydrogel to NO₂ did not deteriorate even after 9 months. This work may open the door to the fabrication of highly deformable and high-performance gas sensors using a family of ionic conductive hydrogels.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b17437.

XPS spectra and elemental analysis of DN hydrogel; SEM image of the DN hydrogel; digital images displaying the DN and DN-Gly hydrogels stretched to different strains; photographs showing the deformability, conductance, and water retention capability of the DN hydrogel; investigation of the electromechanical property of the DN hydrogel; response curves of the DN and DN-Gly hydrogel sensors to NO₂ with different concentrations; plots of the signal recovery percentages of the DN and DN-Gly sensors versus NO₂ concentrations; calculation of sensitivity, noise level and LOD; comparison between different NH₃ sensing materials in terms of response, stretchability, and transparency; and dynamic responses of the DN hydrogel sensor to different gaseous chemicals (PDF)

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