A Highly Sensitive and Flexible Metal–Organic Framework Polymer-Based H\(_2\)S Gas Sensor

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ABSTRACT: We report the fabrication of a novel metal–organic framework (MOF)–polymer mixed-matrix flexible membrane for the detection of hydrogen sulfide (H\(_2\)S) gas at room temperature. This high-performance gas sensor is based on MOF-5 micro-particles embedded on a conductivity-controlled chitosan (CS) organic membrane. The conductivity of the organic membrane is controlled by blending it with a glycerol ionic liquid (IL) at different concentrations. The sensor showed a remarkable detection sensitivity for H\(_2\)S gas at a concentrations level as low as 1 ppm at room temperature. The MOF-5/CS/IL gas sensor demonstrates a highly desirable detection selectivity, fast response time (<8 s), recovery time of less than 30 s, and outstanding sensing stability averaging at 97% detection with 50 ppm of H\(_2\)S gas. This composite having high sensitivity, low-power consumption, and flexibility holds great promise for addressing current challenges pertinent to environmental sustainability.

1. INTRODUCTION

In recent years, the demand for high-performance gas sensors in hostile environments has been of paramount importance owing to the significant increase in the levels of air pollution. Human society has sustained immense damage because of the release of toxic and hazardous gases from industrial environments. Some gases have nonlethal effects on the human system, whereas others, when exposed to even in the order of few parts per million (ppm) concentration, cause effects ranging from respiratory problems to eventual death.\(^1\)–\(^4\) Therefore, highly sensitive, stable, and selective gas sensors would assist in tackling these health and environmental issues.

One of the most potentially hazardous gases is hydrogen sulfide (H\(_2\)S), which is colorless, flammable, highly corrosive, extremely toxic, and potentially lethal even in small doses.\(^5\)–\(^7\) In natural environments such as crude petroleum, natural gas, some mineral rock, hot spring, and landfill environments,\(^8\)–\(^10\) when bacteria in the organic materials or human/animal waste breaks down in the absence of oxygen, H\(_2\)S gas is evolved. Some of the industries that produce substantial amounts of H\(_2\)S gas are wastewater treatment, tanneries, paper mills, glue and dye production, the mining industry, construction,\(^10\) and the drilling and refining of natural gas. Being heavier than air, H\(_2\)S settles in low-lying and enclosed spaces, making it a potentially dangerous environment.

For the past few decades, various gas-detection systems have been used to monitor toxic and volatile organic vapors. Among them, electrically transduced gas sensors based on changes in the resistance or conductivity method, in line with the chemiresistive principle, have received much interest because of their simple technique, low cost, miniaturization, and high sensitivity.\(^11,12\) Enormous efforts have been devoted to further enhancing the sensing performances by studies on both active sensing materials and electrode device fabrication. Among various materials, metal-oxide-based gas sensors have been the prime choice for researchers because of their simplicity in the synthesis and fabrication of high-performance gas-sensing devices.\(^13\)

Despite extensive research on gas sensors made up of metal-oxide semiconductors, their existing bottlenecks of relatively low selectivity and high operating temperatures (100–500 °C) still pose a great challenge. To overcome these circumstances, various strategies have been developed to improve the gas-sensing properties, including the exploration of new and novel materials.

Recently, metal–organic frameworks (MOFs) have emerged as a new class of crystalline, porous, inorganic–organic hybrid materials composed of metal clusters and/or ions linked with
organic ligands.\textsuperscript{14−16} MOFs bearing tunable pore environments, flexible structures, and the ability to exhibit selective gas-adsorption capability\textsuperscript{17} are suitable for gas-sensing applications. MOFs have been demonstrated to be splendid platforms for host–guest chemistry,\textsuperscript{18} with a wide range of applications, including gas sensors operating at various temperatures and sensitivity levels.\textsuperscript{18−21}

MOFs crystallize either in the single-crystal form or in the powder form, which in turn hinders the ability of being dispersed in an analyte solution to optimize the interaction between MOFs and the test gas as the sensors developed in the powder form record significant errors.\textsuperscript{12,18,22} The development of MOFs into membranes exhibits challenges (e.g., MOF synthesis in bulk amounts and the growth conditions for the membranes),\textsuperscript{21,23} and the architectural rigidity nature of the MOFs prevents them from subsequent device manufacture.\textsuperscript{24} In order to deal with these difficulties, there has been ample progress has been made in the technology involving the fabrication of thin films or membranes doped with MOFs for sensing applications.\textsuperscript{25−27} The incorporation of MOFs as nano- and/or microparticles into polymer matrices for the fabrication of sensor membranes has been proven to be a viable strategy for the purpose of gas sensing.\textsuperscript{14,20,28}

Recently, our research group has demonstrated that chitosan (CS) polymer, mixed with glycerol as an ionic liquid (IL), has a detection limit of 15 ppm of H\textsubscript{2}S gas.\textsuperscript{29} However, because of the dense structure, the number of active sites for detecting H\textsubscript{2}S in CS polymer is relatively low. Unlike polymers, MOFs have been shown to exhibit high adsorption selectivity toward many gases; therefore, we think that the combination between suitable MOFs and CS polymer mixed with glycerol would be promising materials for H\textsubscript{2}S-sensing applications. In this study, we particularly aim at exploring the possibility of mixing MOF-5 powder with CS polymer for improving the sensing of H\textsubscript{2}S. This work demonstrates the fabrication of a novel MOF–polymer mixed-matrix flexible membrane for the detection of H\textsubscript{2}S gas at room temperature with a detection limit of 1 ppm, an outstanding result attributed to the synergistic effect of MOF-5 and chitosan/glycerol. Especially, MOF-5 powder is incorporated within a conducting polymer matrix to form a membrane denoted by CS/IL/MOF-5, which has been investigated for H\textsubscript{2}S gas sensing. Impressively, the sensor records sensitivity as low as 1 ppm of H\textsubscript{2}S gas at room temperature, while being extremely stable over long-term exposure, as recorded in the stability measurements conducted for over 21 days. The sensor was also highly selective to H\textsubscript{2}S over other test gases, while exhibiting excellent repeatability. The sensor records an impressive response time of less than 8 s and has an extended advantage of having a low bias voltage of 120 mV.

H\textsubscript{2}S gas-sensing employing MOF-5 along with a polymer composite membrane matrix has not been attempted to the best of our knowledge. The enhancement of the sensing capability of the sensor towards H\textsubscript{2}S gas, in comparison to the other test gases after the incorporation of MOF-5, has been achieved by partially breaking down the three-dimensional (3D) hierarchical structure without compromising its structure and composition. The partial breakdown was achieved by manually grinding the powder using a standard mortar and pestle. The enhancement of the detection limit can also be due to the increase in the surface area of MOF-5, which resulted from the grinding of the as-synthesized powder. The flexibility of the fabricated membrane, along with its requirement of very low biasing voltage, makes it an ideal candidate for the production of the sensor.

2. RESULTS AND DISCUSSION

2.1. Structural Characterization. Figure 1 shows the powder X-ray diffraction (PXRD) patterns of activated MOF-5 coarse and fine powders as compared with their simulated PXRD pattern.

![Figure 1. PXRD patterns of coarse and fine MOF-5 powders as compared with their simulated PXRD pattern.](https://doi.org/10.1021/acsomega.1c02295)
between the resistance of the sensor in N2 gas, the measured current decreased to its initial values within 30 s, which demonstrates the reversibility of the sensor.

The response of the sensor to H2S gas concentrations and as a function of time at room temperature. The inset shown in Figure 5 represents the plot of current vs the gas concentration. The current signal measured records a change as the exposed gas concentration is varied. The data display that there was a proportional increase in the measured current as the gas concentration increased. As the gas flow was stopped and the test chamber was flushed with N2 gas, the measured current decreased to its initial values within 30 s, which demonstrates the reversibility of the sensor. The response of the sensor (S%) is measured as the difference between the resistance of the sensor in N2 gas (Rg) and the resistance measured in sample target gases (Rs), as shown in eq 1.

\[ S (\%) = \frac{R_g - R_s}{R_g} \times 100 \]  

Furthermore, the sensors were subjected to long-term stability and reproducibility tests, with the sensor being exposed to 50 ppm of H2S gas for 5 cycles with flushing of N2 gas between each exposure. Figure 6A shows the long-term stability of the sensor over the period of 21 days. It can be noted that the response displays excellent repeatability and a slight increase in the error bars. The response of the sensor is in the region of 96–98% for 50 ppm of H2S gas with the standard error being less than 1%, indicating excellent stability and reproducibility of the sensor.

Figure 6B displays good repeatability of the sensing membrane with negligible fluctuation in the initial current values. Considering that we are only taking into account the difference between the current values for the gas on and off states, the fluctuation in the initial current can be neglected.

The selectivity of the fabricated sensor was investigated by exposing the sensor to 100 ppm of H2S, H2, C2H4, and CO gases. Figure 7 shows the response of the sensor to the mentioned ppm of the gases at room temperature. The figure reveals that the sensor exhibits weaker responses to the CO, H2, and C2H4 gases compared to the H2S gas. Therefore, it can be concluded that the sensor exhibits excellent selectivity toward H2S gas over the other test gases.

Another vital parameter for the sensor is the response time, which is defined as the time taken by the sensor to reach 90% of its detection efficiency. The response time of the sensor was averaged at 8 s for 100 ppm H2S, with the detection response of ~98%. Table 1 shows the comparison of the response of the sensor under study with those reported in the literature. Because the sensor operates at room temperature and has a 120 mV biasing voltage, the interface required for field operation becomes quite simple and portable.

2.5. Gas-Sensing Mechanism. Being acidic, H2S gas facilitates the sensing mechanism by the transfer of a proton among the acidic gas molecules and basic amino groups from the unfinished chitosan chains. The sensing mechanism for the CS + IL polymer films has been previously outlined, where the combination of CS and IL provides both amino groups and hydroxyl groups with nonbonding electrons on N, and O atoms, respectively. These atoms, therefore, facilitate the proton conductivity throughout the membrane matrix. MOF-S, on the other hand, has a longer linker and a larger pore size with a high number density of MOF-5 being 2.46 × 1028 atoms m−3, and it is characterized by a highly porous architecture with a special cage—bridge structure, which has been shown to enhance microscale energy transport. The chemical structure of MOF-5 ([Zn4O(BDC)3]n) shows the presence of one O atom per every Zn oxo cluster and four O atoms per every BDC linker molecule. The multitude of these oxygen atoms with nonbonding electrons provides extra sites of interactions with the H2S acidic protons. Hence, the presence of well-dispersed MOF-5 nanoparticulates within the CS-IL matrix boosts the transportation of the H2S acidic protons across the membrane and throughout the open porosity of the MOF-5 hierarchical structure, as shown in Figure 8. It is, therefore, the synergistic effect of the conducting components of the proposed nanocomposite membrane that explains its high efficiency and sensitivity toward H2S gas. It should be noted that when the sensing test is conducted in the absence of MOF-S, the sensing performance can only reach 15 ppm of H2S. This clearly indicates the importance of having a porous structure in the composite. We think that the pore structure, pore size and shape, polarization of the framework, and/or the kinds of metal-oxide clusters strongly influence the H2S-sensing property. All of these need to be systematically investigated in future studies. However, our work, as a proof-of-concept of using a composite MOF/CS/IL for this purpose, paves the way for further development of better-performance sensors based on MOFs.
3. CONCLUSIONS

In this work the CS + IL membrane doped with 2 wt % MOF-5 was successfully fabricated for H2S gas-sensing applications. The addition of MOF-5 enhanced the sensing capability toward H2S gas as low as 1 ppm at room temperature. The enhancement can be attributed to the increased surface area of MOF-5 upon grinding, while maintaining the interconnected porosity. The excellent selectivity, stability, and reproducibility results show that the sensor membranes are very reliable and have a significant affinity toward H2S among the other test gases. Furthermore, the sensor operates at room temperature and does not require any heating element, which significantly reduces the power consumption and fabrication costs. The sensor with its detection capability of 1 ppm and fast response time (<8 s) has proficient industrial applications for monitoring air pollution.

4. MATERIALS AND METHODS

4.1. Materials. Zinc nitrate hexahydrate (99%), 1,4-benzenedicarboxylic acid (H2BDC) (98%), N,N′-dimethylformamide (DMF) (99.8%), and dichloromethane (DCM) (99.8%) were purchased from Sigma Aldrich and used without further purification. Chitosan (Mw = 50,000–190,000 Da) (≥ 75%) and acetic acid were purchased from Polysciences.
Glycerol, as an IL (99.5%), was purchased from Quarek Corp company. All chemicals were used without further purification.

4.2. Fabrication of the MOF-5/CS/IL Membranes. In a typical synthesis, zinc nitrate hexahydrate (1.8 g, 6.1 mmol), H$_2$BDC (0.33 g, 2.0 mmol), and DMF (50 mL) were thoroughly blended in a 100 mL Pyrex tube. The sealed tube was heated in an oven at 100 °C for 42 h. After the time elapsed, colorless cubic crystals were obtained on the sealed tube walls. The sealed tube was then removed from the oven and allowed to cool to room temperature. After cooling, excess was heated in an oven at 100 °C for 42 h. After the time elapsed, colorless cubic crystals were obtained on the sealed tube walls. The sealed tube was then removed from the oven and allowed to cool to room temperature. After cooling, excess gas was removed by purging with N$_2$ gas. The crystal was then filtered and washed with DMF, and then dried in a vacuum oven at room temperature.

Table 1. Sensor Performance Comparison with the Literature Reported Values

| sensor/material               | optimum operating temperature (°C) | response (S%) | response time (s) | ref  |
|-------------------------------|-------------------------------------|---------------|-------------------|------|
| MOF-5/CS/IL membrane          | RT                                  | 91% at 100 ppm| <8                | this work |
| CS-IL film                    | 80                                  | 200% at 100 ppm| >15               | 29   |
| polyaniline nanofiber          | 25                                  | 20% at 10 ppm | ~66               | 32   |
| CoO/In$_2$O$_3$ heterostructure| 70                                  | 230% at 5 ppm | <10               | 33   |
| networks of WO$_3$ nanoparticles| 300                                 | >100% at 50 ppm| >2                | 22   |
| Au nanosphere arrays with silver coating | 40 | 2 μM |              | 34   |
| Cu-doped ZnO (CZO) films       | 250                                 | 2.5 ppm       |                  | 35   |

Figure 4. N$_2$-sorption isotherms of fine and coarse MOF-5 powders.

Figure 5. Electrical current response of the MOF-5/CS/IL membrane as a function of time and H$_2$S concentration, measured at room temperature. Inset: response for the corresponding gas concentration.

Figure 6. (A) Stability performance of the MOF-5/CS/IL membrane at room temperature for 21 days and (B) reproducibility of the MOF-5/CS/IL membrane at room temperature.
solvent was decanted, and the remaining crystals were washed
with anhydrous DMF. Solvent exchange was performed using
DCM (3 × 20 mL) by soaking the crystals in the solvent for 3 h, followed by solvent decantation. Subsequently, the prepared
sample was then activated at 150 °C under vacuum for 24 h.

CS stock solution was prepared by dissolving 2 g of CS in
3% acetic acid by stirring at room temperature for 24 h. The
CS stock solution (5 mL) was taken and mixed with 5 vol % of
IL29 and 2 wt % of MOF-5. The formed blend was stirred at 70
°C at 1100 rpm for 15 min, followed by casting into a Petri
dish for drying in a vacuum oven at 70 °C for 12 h. A uniform
flexible membrane was obtained, as shown in Figure 9. The
thickness of the membrane was measured using a screw gauge
and found to be 0.12 mm.

It should be mentioned that the presence of coarse MOF-5
particulates was reflected in the high surface roughness of the
prepared composite membrane. Accordingly, the as-prepared
mixture was subjected to grinding using a mortar and pestle in
the presence of ethanol for 4 h. This was followed by drying
using an IR lamp for 15 min. The fine powder was also
subjected to structural and morphological characterization.

4.3. Characterization. MOF-5 powder was analyzed for its
structural and morphological characteristics. PXRD studies
were carried out using a Rigaku, MiniFlex 600-C instrument,
USA, with a CuKα X-ray at a scan rate of 2°/min and within a
range of 5–90°. A Thermoscientific Quattro S SEM instru-
ment (USA) was used at an operating voltage of 15 kV to
study the morphology of the MOF-5 powder, before and after
grinding, as well as the morphology of the fabricated
membranes. FT-IR studies were performed using Thermo
Nicolet, NEXUS, 470 FT-IR instrument, using the KBr disk
method over a wavelength range of 400–4000 cm⁻¹. TGA
studies were carried out using TGAS500 (TA instruments,
USA).

4.4. Sensor Fabrication and H₂S Gas-Sensing Tests.
The MOF-5/CS/IL membrane was diced into a 1 × 1 cm
piece and mounted between a copper plate (1.5 × 1.5 cm) and
a 0.8 × 0.8 cm stainless-steel grid (anticorrosive against H₂S),
with a grid size of 250 × 250 μm, which serve as the bottom
and top electrodes, respectively, forming the sensor. The layers
were bound together with temperature-resistive Kapton tape.
Figure 10A,B shows the connections made on the sensor. The
sensor was fixed on a heating stage inside a Teflon chamber, as
shown in Figure 10C. The gases tested were diluted with N₂
gas and injected into the chamber using Bronkhorst mass flow
controllers (MFCs) that were kept inside a fume hood at room
temperature. The test chamber was sealed to maintain a
nonhumid atmosphere. For the gas-response test, a constant
bias voltage of 120 mV was applied between the sensor
electrodes, and its electrical current signal was measured at
different H₂S gas concentrations using a Keithley Instruments
source measurement unit (KI 236). The MFC and KI 236
were interfaced to a computer using the LABVIEW software.

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