Silver Nanoparticles anchored UiO-66 (Zr) Metal-Organic Framework (MOF) based Capacitive H₂S Gas Sensor

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Silver Nanoparticles anchored UiO-66 (Zr) Metal-Organic Framework (MOF) based Capacitive H₂S Gas Sensor

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Abstract:

Hydrogen sulfide (H_2S) is a highly poisonous gas that, when in a work place, must be identified immediately at concentrations greater than 10 ppm. Although there are numerous reports on sensing H_2S gas using various techniques and approaches, there still exist a gap in terms of limit of detection (LOD) and feasibility. In this work, we demonstrate capacitive H_2S sensing for the first time using metal organic frameworks (MOFs) decorated with Silver oxide (Ag_2O) nanoparticles as the sensing material. The nanoparticles were deposited on three MOFs ($\text{UiO-66}(\text{Zr})$ BDC, $\text{UiO-66}(\text{Zr})$ BDC- NO_2 , and $\text{UiO-66}(\text{Zr})$ BDC- N_3) using impregnation technique. The sensing materials were characterized for morphology using x-ray diffraction, scanning electron microscopy, and x-ray photoelectron spectroscopy techniques. The synthesized MOFs were coated on interdigitated electrode capacitors as dielectric material and a comparison of their sensing properties are presented among which $\text{UiO-66}(\text{Zr})$ BDC- NO_2 loaded with Ag_2O showed the highest sensitivity towards H_2S . The optimized MOF- Ag_2O composite demonstrated an experimental LOD of 1 ppm of H_2S at room temperature showing a high chemical absorption affinity towards H_2S . The work presented here is promising for developing sensitive H_2S sensors and in addition paves the way to explore and develop other possible MOF based composite materials for gas sensing application.

Keywords: Hydrogen Sulfide; $\text{UiO-66}(\text{Zr})$; Metal Organic Frameworks; Capacitive sensor; Ag_2O nanoparticles

1. Introduction

Rapid development of various chemical, pharmaceutical industries, oil and natural gas refineries have led to increased emanation of hazardous gases, toxic pollutants, and volatile organic compounds (VOCs) into the atmosphere. This is currently the subject of serious concern owing to their adverse effects to human health and environment. Among many hazardous gases, hydrogen sulfide (H_2S), which is also known as chemical asphyxiation gas is a highly flammable and toxic gas. This is because it reacts rapidly with hemoglobin in the blood causing impediment in the flow of oxygen into the tissues and vital organs of human body. At lower concentrations, H_2S gas can be smelled as rotten egg and at higher concentrations (>100 ppm) the odor of H_2S disappears, leading to false alarms by the human olfactory system and may even lead to death.¹⁻³ According to the American Conference of Government Industrial Hygienists (ACGIH), the threshold limit value (TLV) for H_2S has been set to 10 ppm for 8 h of exposure.¹ However, the Scientific Advisory Board on toxic air pollutants, USA has set the guidelines for the potential danger of H_2S and its acceptable level of concentration to humans in the range of 20-100 ppb.⁴ In the light of associated potential hazards of H_2S on human health and the environment, it is therefore extreme significance to develop smart and effective gas sensing technologies for the early monitoring and rapid detection of H_2S . Previously, many approaches have been employed for the detection of H_2S including gas chromatography (GC)⁵ and Raman spectroscopy techniques.⁶ The former one, however, is not widely accepted due to their multi-step testing procedure making them inconvenient to monitor with varying H_2S concentration according to ambient conditions. Similarly, the later one is rather time-consuming and involves tedious sample preparation protocols. On one hand, commercial H_2S gas sensors are available based on

electrochemical⁷ and calorimetry detection techniques,⁸ but they are either expensive and/or difficult to miniaturize and integrate with readout electronics. On the other hand, for decades, metal oxides and their composites based gas sensors have been widely used for the detection of many environmental pollutants and toxic gases including H₂S. However, they have several drawbacks such as poor selectivity and mostly require high operating temperature (100-500 °C).⁹⁻¹² Therefore, the development of industry driven, alternative gas sensing materials with high selectivity and sensitivity operating at room temperature (RT) is necessary for practical application.

Fusion of organic linkers and inorganic metal ions by self-assembly has led to a new class of crystalline materials with high porosity called metal organic frameworks (MOFs) and has emerged as one of the research hotspot for designing new functional porous materials.¹³ Thanks to their outstanding characteristics such as structural diversity, excellent tunability of pore size, high surface area, ultra-high porosity, flexibility, open metal sites, high thermal (200-500°C) and chemical stability,¹⁴⁻¹⁶ MOFs have encouraged researchers and scientists to explore in diverse applications such as catalysis,¹⁷ separation and adsorption,^{18, 19} gas sensing,²⁰⁻²² bio-sensing,²³ and super-capacitors.²⁴ In particular, recent advances in MOFs are shown to be promising for developing low cost, ultra-fast, highly sensitive and selective gas sensors. Our group has previously investigated the gas sensing properties of various MOFs for many toxic gases and VOCs including H₂S.^{4, 25-27} Nonetheless, all these MOFs based gas sensors are one-component systems (non-composites) and the study on improving their sensitivity is still in a bottleneck. Hence, one of the possible ways to develop a highly sensitive gas sensor that could operate at RT is to integrate two different components with different catalytic functionalities such as MOFs and noble metal nanoparticles (NPs) into a single component. The newly formed functional material

could have enhanced sensing characteristics when compared with its single counterpart. Noble metal NPs are known to have excellent catalysts properties and have been utilized on MOFs to enhance their catalytic and gas sensing properties.^{17, 28} Among the many kinds of MOFs, zirconium based MOFs such as University of Oslo (UiO-66-Zr) has gained much attention due to their inherent properties and ability to incorporate reactive metal centers, making them promising candidates for many applications. Interesting to note that the physical and chemical properties of UiO-66(Zr) can be judiciously tuned by functionalizing with different functional groups or linkers.²⁹ Owing to the above fascinating features, UiO-66 (Zr) can be used as promising materials for the gas sensing study. Various transduction mechanism such as optical,³⁰ thermal,³¹ magnetic,³² surface acoustic wave guide (SAW),³³ resistance,³⁴ resonance,³⁵ and capacitive^{4, 24-26} have been employed for the detection of target gaseous analytes. Among them, interdigitated electrode (IDE) capacitive transducer is one of the most investigated technique owing to its miniature size, low-cost, low temperature independence, easy to integrate with read circuits, and high sensing performances features.⁴

In this work, we propose for the first time the integration of UiO-66 (Zr) MOF (synthesized by a facile method) and Ag₂O NPs to form Ag₂O@UiO-66 composite for developing H₂S gas sensing material. The novelty of current work is the anchoring of Ag₂O NPs onto UiO-66 (Zr) MOFs with various modified functional groups (N₃, NO₂). We fabricated the entire IDE sensor platform on top of Si/SiO₂ substrate and deposited it with our as prepared Ag₂O-UiO-66 composite materials and investigated their H₂S gas sensing properties. Further, material characterizations like field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction (PXRD) are carried out on these sensing materials to confirm their morphology, oxidation states, and crystallinity, respectively. Ag₂O-UiO-66(Zr)-

BDC-NO₂ combination was seen to have the highest sensitivity with an experimental limit of detection (LOD) of 1 ppm.

2. Experimental details

2.1. Chemicals and instruments

Chemicals such as HCl, Methanol, terephthalic acid (1,4-benzenedicarboxylic acid or H₂BDC), 2-aminoterephthalic acid (NH₂-H₂BDC), 2-nitroterephthalic acid (NO₂-H₂BDC), anhydrous zirconium chloride (ZrCl₄), silver nitrate (AgNO₃), acetonitrile (CH₃CN), sodium nitrite (NaNO₂), sodium azide (NaN₃), and dimethylformamide (DMF) were purchased from Sigma Aldrich and were used without any further purification. The PXRD and FESEM (and EDAX) of the all MOFs were recorded on Bruker D2 Phaser and Zeiss Merlin FESEM, respectively. XPS analysis was done with Kratos analytical Axis Ultra. The samples were prepared by drop costing on silicon wafer for recording XPS, FESEM, and EDAX analysis. N₂ adsorption-desorption measurements of UiO-66(Zr)-NO₂ and Ag₂O@UiO-66(Zr)-NO₂ were performed volumetrically at 77 K in the pressure range of 0 to 760 Torr using a Quantachrome Autosorb-iQ gas sorption analyzer. A liquid N₂ bath was used to maintain a temperature of 77 K during the measurements. Ultrapure (99.999%) N₂ and H₂ gases were used for the measurements, prior to which, the as-synthesized samples were activated by immersing them in dry chloroform at ambient temperature for 24 h followed by evacuating at 130 °C for 15 h under vacuum. In order to obtain samples completely free of guest molecules, UiO-66(Zr)-NO₂ and Ag₂O@UiO-66(Zr)-NO₂ were again degassed at 180 °C under a dynamic vacuum of 10⁻³Torr.

2.2 Synthesis of sensing materials

2.2.1 Synthesis of UiO-66(Zr) BDC

UiO-66(Zr)-BDC was synthesized by using a previously reported process with some modifications.³⁶ Typically, a mixture of H₂BDC (123 mg) and ZrCl₄ (125 mg) were dissolved in 15 mL DMF and 1 mL of HCl was further added to the solution and was followed by stirring for 1 h. The above solution was transferred and sealed in a Teflon-lined stainless steel vessel (17 mL) and heated in an oven at 120 °C for 24 h. The white crystalline powder was cooled to room temperature, isolated by centrifugation technique, and washed multiple times with DMF. The obtained powder was dipped in MeOH for 4 days to get DMF free MOF followed by activation by annealing at 100 °C for 12 h in a vacuum chamber.

2.2.2 Synthesis of UiO-66(Zr) BDC-NO₂:

UiO-66(Zr)-BDC-NO₂ was synthesized by slight modification of a previously reported protocol.³⁶ In brief; a mixture consisting of 146 mg of H₂BDC-NO₂ and 162 mg of ZrCl₄ was dissolved in 8 mL of DMF and stirred for one hour. The above mixture solution was transferred and sealed in a Teflon-lined stainless steel vessel (17 mL) and heated in an oven at 120 °C for 24 h. The white crystalline powder was cooled to room temperature, isolated by centrifugation, and then by washed multiple times with DMF. The obtained powder was dipped in MeOH for 4 days to exchange DMF solvent from the MOF and was then activated at 100 °C for 12 h in a vacuum chamber to get solvent free pores of MOF.

2.2.3 Synthesis of UiO-66(Zr) BDC-N₃:

The synthesis of UiO-66(Zr) BDC-N₃ was followed according to a previous report but with some modification.³⁷ Initially, the UiO-66(Zr)-BDC-NH₂ was synthesized using the process previously reported.³⁷ Then, the activated UiO-66(Zr)-NH₂ (300 mg) was dissolved in H₂O: HCl (1:1, 2

mL) at 0 °C in a 50 mL beaker. 0.198 mg of NaNO₂ was dissolved in 6 mL of H₂O and added drop wise to the UiO-66(Zr)-NH₂ mixture and stirred for 30 min. The solution was then added to an ice cold solution of NaN₃ (0.156 g in 6 mL of H₂O) in a 150 mL of round bottom flask and stirred further for 20 h at room temperature. The resultant mixture was filtrated by applying vacuum pump and was then washed with ice cold water for 4 times. In order to remove the unreacted starting material, the solid residue was exchanged with H₂O for 2 days. The solid precipitate was collected and activated at 120 °C to yield UiO-66(Zr)-N₃.

2.3 Synthesis of Ag₂O@MOF:

The Ag₂O@MOF composites were prepared by impregnation method.³⁸ Typically, 50 mg of as obtained activated MOFs (UiO-66(Zr) BDC, UiO-66(Zr) BDC-NO₂, and UiO-66(Zr) BDC-N₃) powders were immersed in CH₃CN (8 mL) containing 30 mg of silver nitrate and the mixture was stirred at room temperature for 4 h. After the impregnation, the suspension was centrifuged to separate the solid MOF and was washed thrice with CH₃CN. The solid AgNO₃ metal salts were encapsulated in MOF powder and thereafter were annealed at 130 °C for 2 h in air to form the desired Ag₂O@MOF composite with a temperature ramp rate of 2 °C/min. The methodology used for preparing UiO-66 (Zr) MOF anchored with Ag₂O nanoparticles is schematically illustrated in Fig. 1.

2.4 Sensor fabrication and characterization:

We fabricated IDE substrates as reported in our earlier findings.^{27, 39} 5 mg of MOFs and their composites were added to the 1 mL of DMF solvent and stirred for 3 hours at 1000 rpm. Subsequently, obtained MOF DMF mixtures (2 µL) were deposited on top of the IDE structure followed by annealing on a hotplate at 90 °C for 20 minutes. The fabricated sensors were wire

bonded with gold wire on to a printed circuit board (PCB) that was optimized for our IDE substrate design. Each of the sensors mounted PCB was placed in the gas chamber for analysis. As shown in Fig. 2, LCR meter was used to probe the capacitance of the sensor during dry air purge. Once the baseline was achieved, H_2S gas of known concentration was introduced into the test chamber in a controlled way through MFCs and sensor was characterized at multiple H_2S concentration levels. The base H_2S gas used was of 100 ppm in concentration and diluted to concentrations ranging from 1ppm to 100 ppm by split flow method (by controlling flow rates of the MFCs of dry air cylinder and H_2S gas cylinder).

Fig. 1: Schematic illustration of synthetic strategies of UiO-66 (Zr) MOFs and anchoring of Ag_2O NP@MOFs.

Capacitive response was extracted by applying an AC voltage bias fixed of 0.5 V_{RMS} at 100 kHz for all samples. The frequency of the voltage was optimized for the device dimensions as per our previous studies.⁴⁰ LabVIEW was used to control the interface with LCR meter and MFCs in the gas sensor characterization setup. Furthermore, XPS analysis was also done to study the Ag oxidation state and to detect the presence of Sulphur on samples before and after exposing the sensing material to H₂S gas.

Fig. 2: Schematic diagram of gas sensor setup with the actual chip mounted on PCB.

3. Results and discussion:

3.1 Morphological and structural characterization

The characterization of as prepared materials was carried out by PXRD (Fig.3) and FESEM (Fig.4) to analyze the morphology and structural aspects. Fig. 3 shows the XRD peaks of pristine

UiO-66 (Zr)-NO₂ and of Ag₂O@UiO-66 (Zr)-NO₂. The XRD pattern of both the materials show phase purity and good crystallinity. UiO-66 (Zr)-NO₂ and Ag₂O@UiO-66 (Zr)-NO₂ MOFs reveal that the XRD peaks at $2\theta = 7.15^\circ, 8.35^\circ, 11.80^\circ, 13.90^\circ, 14.60^\circ, 17.01^\circ, 18.35^\circ, 18.96^\circ, 20.60^\circ, 22.05^\circ, 24.03^\circ, 25.54^\circ, 27.86^\circ, 29.56^\circ, 30.60^\circ, 32.01^\circ, 32.92^\circ, \text{ and } 35.20^\circ$ that are indexed to the corresponding planes of (111), (002), (022), (113), (222), (004), (133), (024), (115), (044), (135), (006), (335), (444), (117), (246), (355) and (008), respectively.⁴¹⁻⁴³ However, there are no diffraction peaks of Ag₂O or Ag that are visible in the XRD patterns. This may be due to the low content of Ag₂O loadings and/or due to the small dimensions of Ag₂O nanoparticles in Ag₂O@UiO-66 (Zr)-NO₂ sample.

Fig. 3: The PXRD patterns of UiO-66 simulated, UiO-66(Zr)-NO₂ and Ag₂O@UiO-66 (Zr)-NO₂ as synthesized MOFs with high phase purity and crystalline.

Fig. 4 shows the FESEM micrographs of the as prepared UiO-66 (Zr) and their composites. Fig. 4(a) is the FESEM micrograph of the UiO-66 (Zr), which shows a smooth surface with regular octahedral particles in the range of 50-100 nm. Fig. 4(b) shows the FESEM micrograph of Ag₂O@UiO-66 (Zr) composite, which shows a smooth surface with agglomerated MOF particles. The agglomerated particles are composed of many primary MOF particles in the range of 50-100 nm. Fig. 4(a). There is no any detectable change in the MOF's morphology after the Ag₂O nanoparticles were anchored on the surface. However, numerous tiny Ag₂O nanoparticles are clearly visible and uniformly distributed throughout the surface of UiO-66. The particle size of Ag₂O nanoparticles are found to be in the range of 5-20 nm. Fig. 4(c) and (d) are the FESEM micrographs of the UiO-66 (Zr)-NO₂ and Ag₂O@UiO-66 (Zr), respectively. Fig. 3(d) clearly depicts that the Ag₂O nanoparticles are distributed on the surface of UiO-66 (Zr)-NO₂ along with presence of agglomerated Ag₂O particles. EDAX analysis was carried out to ascertain the elemental composition of the prepared sensing materials. Fig. 4(e) shows the EDAX analysis and as expected has the presence of elements such as C, N, Ag, Zr, and O in Ag₂O@UiO-66 (Zr)-NO₂.

The corresponding low temperature adsorption isotherm for N₂ (77 K) exhibit significant uptake which confirms permanent porosity and shows reversible type I isotherms for both UiO-66 (Zr)-NO₂ and Ag₂O@UiO-66 (Zr)-NO₂ with uptake value of 324.66 mL/g and 153.88 mL/g respectively (shown in Fig.5). This further confirms the decrease in N₂ adsorption uptake due to encapsulation Ag₂O nanoparticles. BET (Brunauer–Emmett–Teller) surface areas were calculated from the N₂ adsorption profile at 77 K as per guide lines of Requrol, Snurr and Walton et al. which found to be 819.889 m²/g for UiO-66 (Zr)-NO₂ and 359.213 m²/g for Ag₂O@UiO-66

(Zr)-NO₂. Also, the total pore volume for UiO-66 (Zr)-NO₂ and Ag₂O@UiO-66 (Zr)-NO₂ were found to be 0.5022 cm³/g and 0.2380 cm³/g simultaneously.^{44, 45}

Fig. 4: The FESEM micrograph of (a) UiO-66(Zr), (b) Ag₂O@UiO-66, (c) UiO-66(Zr)-NO₂, and (d) Ag₂O@UiO-66(Zr)-NO₂. (e) EDAX analysis of Ag₂O@UiO-66(Zr)-NO₂ composite.

X-ray photo-spectroscopy (XPS) was carried out on H_2S exposed UiO-66(Zr)-NO_2 and $\text{Ag}_2\text{O@UiO-66 (Zr)-NO}_2$ MOFs to determine the change in the oxidation state of Ag in Ag_2O nanoparticles. In the XPS graphs, the AH corresponds to $\text{Ag}_2\text{O@UiO-66 (Zr)}$ exposed to H_2S and NAH corresponds to $\text{Ag}_2\text{O@UiO-66 (Zr)-NO}_2$ exposed to H_2S . Fig. 6 (a) shows the Ag_2O $3d_{5/2}$ peak in the structure at a binding energy (B.E) of $368.3 \text{ eV}^{46, 47}$ which is further oxidized to $\text{Ag}_2\text{S@UiO-66 (Zr)-NO}_2$ upon exposure to H_2S gas. Fig. 6 (b) shows no such change in NO_2 for all the cases of $\text{Ag}_2\text{O@UiO-66 (Zr)-NO}_2$ before and after H_2S exposure.

Fig. 5: N_2 Gas adsorption isotherm profile of the a). UiO-66(Zr)-NO_2 and b). $\text{Ag}_2\text{O@UiO-66(Zr)-NO}_2$ at 77 K .

It is obvious that there is lower availability of NO_2 functional groups on the surface compared to Ag_2O but instead are present inside the MOF pores. Hence we believe that due to the conversion of Ag_2O to Ag_2S and the presence of the NPs on the pore opening as well as on the surface of the MOF hinder the H_2S gas from diffusing deeper further to convert NO_2 to NH_2 groups.

Fig. 6: XPS peaks of (a) Ag₂O@UiO-66 (blue in color) and Ag₂O@UiO-66(Zr)-NO₂ (green in color) after exposing to H₂S gas. (b) UiO-66(Zr)-NO₂, Ag₂O@UiO-66(Zr)-NO₂ before (blue in

color) and after (green in color) exposure to H₂S gas. (c). Peaks for sulfur before (blue in color) and after exposure to H₂S.

Hence there is the appearance of NO₂ functional groups binding energy peaks at 406.3 eV in XPS spectra. In case of Ag₂O@UiO-66 (Zr)-NO₂ alone, upon exposing to H₂S gas, it was observed that 2p and 2s peaks of Sulphur are at 225.1 eV and 161.8 eV, respectively as seen in Fig. 6(c). In general, the capacitance of a material is related to its surface area and electrical conductivity, but apart from that, the increase in capacitance can also be attributed to integrated Ag₂O and NO₂ containing functional groups in the MOF.

3.2 H₂S gas sensing measurements

We measured the capacitive characteristics of the different MOFs deposited IDE substrates. Continuous measurements were taken using LCR meter in three phases: (1) during dry air purge, (2) during exposure of H₂S gas, and (3) final purge (to check the effects of desorption of H₂S gas). However, due to intrinsic nature of the MOFs we did not observe any regeneration of the device properties after step 3. Also, we could not revive the device sensing characteristics with repeated annealing (at temperatures >100 °C) on top of a hotplate as well as in vacuum chamber. Here, U, U_N₃, U_NO₂, U_N₃_A and U_NO₂_A correspond to UiO-66 MOFs with no group, with N₃ functional group, with NO₂ functional group, with Ag₂O loaded N₃ functional group, and with Ag₂O loaded NO₂ functional group, respectively. As shown in the Fig. 7, the response to the base free MOF was near zero, whereas, for the MOFs with N₃ and NO₂ functional groups showed low but detectable response. Such a change in response is similar to our previous work on H₂S but with much higher sensitivity.⁴

Fig. 7: (a) Comparison of the response H₂S sensors coated with different sensing materials of MOF and NP@MOF when exposed to 100 ppm of H₂S. (b) Shows the response of UiO-66(Zr)-N₃ and UiO-66(Zr)-NO₂ MOFs.

Ag₂O nanoparticle loaded MOF with N₃ functional group proved to be the most sensitive configuration. We obtained an excellent sensitivity of approximately 90% with the new receptor layer and were 8 times higher than the response of U_N₃_A. The capacitance changes were induced by the MOF layer whereas the sensitivity was enhanced by the Ag₂O nanoparticles in the sensing dielectric material. Thus, the synergistic combination of Ag₂O nanoparticles and NO₂ embedded MOF proved to be a better candidate for detecting low concentrations of H₂S. The higher sensitivity can be attributed to the presence of Ag₂O on the surface thereby leading to increased capacitance compared to the individual UiO-66(Zr)-NO₂. The corresponding mechanism is explained by the transformation of Ag₂O nanoparticle to Ag₂S after the interaction with H₂S gas and is corroborated by the XPS results presented in Fig. 6.^{48,49} Ag₂O NPs increased the adsorption of H₂S gas molecules on the surface of MOF due to catalytic effect and formation of Ag₂S.

In addition, we observed that the capacitive response characteristics are non-regenerative and they tend to remain in the effected state after testing with H₂S gas. We hypothesize that the adsorbed H₂S molecules after the interaction with the MOF and NPs combination tend to remain at the surface of the sensor there by permanently affecting the overall dielectric constant. In support, XPS studies conducted on such surface reveals the presence of Sulphur (2s and 2p) peaks even after the continuous purge with air (Fig. 6(c)). It essentially confirms that the reacting nature of H₂S molecules with the Ag₂O and NO₂ available on the surface of Ag₂O@UiO-66(Zr)-NO₂ and thereby the formation of Ag₂S. Furthermore, the saturation of the capacitance after certain amount of time reveals that not all of the H₂S gas blown into the chamber reacts with MOFs. Also, we observed that the saturation of capacitance depends relatively more on the number of Ag₂O NPs than the MOFs alone. Thus, a synergistic combination of both Ag₂O NPs

and MOFs proved to be successful in the detection of H_2S gas with improved performance. Further, Fig. 8 (a) shows the change in response (%) of the sensor at different concentrations H_2S gas ranging from 1 ppm to 100 ppm for a fixed concentration of receptor layer. we observed a non-linear response below 20 ppm and linear response in the range from 20 ppm to 100 ppm. LOD is an important parameter for any sensor that decides the device's viability.

Fig. 8:(a) Capacitive response of $\text{Ag}_2\text{O}@ \text{UiO}-66 (\text{Zr})-\text{NO}_2$ based sensor at various concentrations of H_2S gas. (b) Time response of $\text{Ag}_2\text{O}@ \text{UiO}-66 (\text{Zr})-\text{NO}_2$ based sensor at 100 ppm of H_2S gas.

Here, we achieved a LOD of 1 ppm for the synergistic combination of silver nanoparticles and UiO-66(Zr)_NO₂. Fig. 8(b) shows the time response of the sensor when exposed to 100 ppm of H₂S gas. The response time was about 3.5 mins. However, the response time here is relatively high due to the limitation of the H₂S gas flowrate (200 sccm). In addition, as stated above, the sensor did not revive when purged with dry air. Overall, the UiO-66(Zr)_NO₂ anchored with Ag₂O nanoparticles is a promising material for developing H₂S gas sensor with high sensitivity and low LOD. Comparison of our results with recently reported H₂S sensor is presented in Table1. It can be seen that capacitive transduction is suitable for room temperature sensing of H₂S. Whereas resistive transduction requires high operating temperature. The device reported here has near-linear compared to most sensors having nonlinear response. The response time is low however is limited due to gas flow rate and test chamber volume. The LOD is comparable to most of the recently reported devices. Overall, the device reported here is promising for developing sensitive H₂S gas sensors.

Table1: Comparison of recently reported H₂S gas sensors.

Ref.	Transduction	Sensing material	LOD	Operating temperature	Response Time	Response type
This work	Capacitive	Ag@UiO-66(Zr)-NO ₂	1 ppm	Room temperature	200 s	Near-linear
4	Capacitive	Fumarate-Based fcu-MOF	100 ppb	Room temperature	900 s	Linear
50	Resistive	Chitosan-Glycerol-WO ₃	15 ppm	40 °C	13.6 s	Nonlinear
51	Resistive	CuO microspheres with CuFe ₂ O ₄ nanoparticles	1 ppm	120 °C	196 s	Nonlinear
52	Chemiresistive	Graphene decorated with Ag	100 ppb	Room temperature	300 s	Linear
53	Resistive	SnO ₂ -CuO	1 ppm	200 °C	5.27 s	Nonlinear
54	Resistive	α-Fe ₂ O ₃	100 ppb	260 °C	30 s	Nonlinear
55	Resistive	CdS + Co ₃ O ₄	5 ppm	Room temperature	12.7	Nonlinear

4. Conclusion

Here, we fabricated an IDE device based capacitive sensor with UiO-66 (Zr) MOF and successfully demonstrated the detection of H₂S gas at low concentration. Decoration of Ag₂O NPs on to the UiO-66-(Zr) based MOFs has slightly improved the response characteristics of the device to H₂S. We also demonstrated the results in comparison with other combinations like UiO-66(Zr)-BDC-NO₂, UiO-66(Zr)-BDC-N₃, Ag₂O-UiO-66(Zr)-BDC-NO₂ and Ag₂O-UiO-66(Zr)-BDC-N₃. Among all the highest sensitivity is achieved with the right combination of Ag₂O and UiO-66(Zr)-BDC-NO₂ MOFs. Limit of detection of the device obtained from the CV analysis for the same combination is 1 ppm. SEM imaging with EDX confirmed the range of the nanoparticles and their concentrations for such minimal response and LOD. Whereas, the XPS analysis provides of the actual mechanism of the interaction of H₂S with the Ag₂O@MOF films detailed understanding. We observed the formation of Ag₂S and the presence of binding sites with the help of Sulphur in its 2s and 2p states. Thus, we achieve a sensitivity of 89% (at 100 ppm H₂S) that is eight times the order of magnitude as compared with the second best combination Ag₂O-UiO-66(Zr)-BDC-N₃. Finally, the versatility of the platform and the uniqueness of the fabrication route provide potential opportunities for developing electronic nose based sensors for a variety of gas phase analytes including VOCs.

Competing interests

The authors declare that they have no competing interests.

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Graphical Abstract:

Metal organic frameworks anchored with metal oxide nanoparticles for the detections of H_2S gas with enhanced sensitivity.