

Enhanced Room-Temperature H₂S Gas Sensing by a Polypyrrole/MoO₃ Heterojunction: Performance and Mechanistic Insights

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Research Article

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Abstract

Hydrogen sulfide is acutely toxic at concentrations routinely encountered in geothermal, petrochemical and wastewater operations, yet conventional metal-oxide sensors require heating to 100–300°C, raising power consumption and introducing an ignition hazard. Here a polypyrrole/MoO₃ composite is shown to detect H₂S at room temperature without these penalties. The composite was prepared by in-situ oxidative polymerisation of pyrrole on MoO₃ nanopowder at a 1:1 mass ratio and deposited on copper interdigitated electrodes. X-ray diffraction confirms retention of the orthorhombic MoO₃ phase (JCPDS 47-1081) alongside amorphous polypyrrole, while selective broadening of the terminal Mo = O stretch in FTIR, the attenuation of that band evidences interfacial charge transfer. Current–voltage measurements reveal a transition from non-ohmic transport in the pristine polymer (217 kΩ) to strictly ohmic conduction in the composite (1.05 kΩ), a 206-fold conductivity enhancement arising from p-type doping of the polymer by the oxide. Both materials show a resistance increase on H₂S exposure, confirming hole-dominated transport. Over 5–250 ppm the composite response exceeds that of the polymer by 2.1–3.0 times, reaching 133% at 100 ppm with response and recovery times of 88 and 58 s. Selectivity coefficients of 2.4–11.1 against ammonia, nitrogen dioxide, ethanol and carbon monoxide reflect the preference of molybdenum for sulfur, and 87.2% of the initial response survives sixty days of ambient operation.

1. Introduction

Hydrogen sulfide (H₂S) is a highly toxic, colorless gas that poses severe occupational and environmental hazards. The Occupational Safety and Health Administration (OSHA) establishes a permissible exposure limit (PEL) of 15 ppm for a 15-minute time-weighted average, with exposure above 100 ppm causing rapid loss of consciousness and death. Industrial activities generate substantial H₂S emissions, particularly in crude oil refining, natural gas processing, geothermal energy production, wastewater treatment, and paper manufacturing [1, 2]. In geothermal fields, H₂S concentrations can exceed 1000 ppm, necessitating real-time continuous monitoring for worker safety. Additionally, anaerobic decomposition in municipal wastewater systems and landfills produces H₂S as a byproduct, requiring environmental monitoring to prevent occupational exposure and atmospheric pollution. Traditional gas-sensing approaches, including electrochemical cells and infrared spectroscopy, suffer from significant limitations: high power consumption, slow response kinetics, limited portability, and prohibitive cost, restricting their deployment in remote or resource-constrained environments [3, 4]. These factors collectively make H₂S detection a critical analytical challenge and an ideal benchmark for evaluating advanced gas-sensing materials.

Metal oxide semiconductors have dominated commercial gas-sensing applications for decades due to their thermal stability, mechanical robustness, low cost, and responsive surface chemistry. Among metal oxides, molybdenum trioxide (MoO₃), an n-type semiconductor with a wide optical bandgap (~ 2.8–3.0 eV) and layered orthorhombic crystal structure, has recently emerged as a promising candidate for gas-sensing applications [5]. The fundamental sensing mechanism of MoO₃ involves oxygen surface

chemistry: atmospheric oxygen adsorbs on the MoO_3 surface and traps conduction electrons, creating an electron-depleted surface region (depletion layer) that increases electrical resistance. Upon exposure to reducing gases such as H_2S , electron-donating reactions occur at the surface, removing adsorbed oxygen and reducing depletion-layer thickness, thereby decreasing overall device resistance [6]. Recent investigations have demonstrated that MoO_3 exhibits moderate H_2S sensitivity at elevated operating temperatures (100–200°C), with response magnitudes typically ranging from 40–70%. However, high-temperature operation increases power consumption, accelerates device degradation, and raises safety concerns in flammable atmospheres. Furthermore, pristine MoO_3 sensors suffer from baseline drift, poor humidity robustness, and limited selectivity against interfering gases such as ammonia and volatile organic compounds [7, 8].

Conducting polymers, particularly polypyrrole, have gained considerable attention in gas-sensing research owing to their tunable electrical properties, facile synthesis, low cost, and inherent room-temperature operability [9]. Polypyrrole is a conjugated polymer formed via oxidative polymerization of pyrrole monomers, yielding a p-doped, electrically conductive material. The gas-sensing transduction mechanism in polypyrrole operates via doping/undoping processes: exposure to reducing gases (e.g., H_2S , ammonia) induces de-doping, decreasing conductivity, while oxidizing gases (e.g., NO_2) increase doping level and conductivity. Polypyrrole-based sensors offer distinct advantages: room-temperature operation (eliminating power-intensive heating), rapid response and recovery kinetics, high sensitivity to trace analytes, and straightforward chemical modification through dopant engineering [10]. However, pristine polypyrrole exhibits critical performance limitations that severely restrict practical deployment: pronounced baseline resistance drift over extended operation due to polymer relaxation and environmental cycling; elevated humidity sensitivity, whereby atmospheric moisture alters the doping equilibrium and baseline resistance, introducing substantial measurement noise; broad analyte response (poor selectivity), as the polymer responds indiscriminately to both reducing and oxidizing species; and thermal instability, with polymer degradation occurring above 150–200°C [11, 12]. These inherent constraints have motivated the development of polypyrrole-based composite structures that synergistically combine the rapid response and room-temperature sensitivity of conducting polymers with the thermal stability and selective chemical reactivity of metal oxides.

Heterostructured composites combining conducting polymers with metal oxides have demonstrated substantially enhanced gas-sensing performance compared to single-component materials. Heterojunction formation at the polymer–oxide interface creates favorable electronic structures and amplifies charge-transfer sensitivity. When an n-type metal oxide (such as MoO_3) contacts a p-doped conducting polymer (such as polypyrrole), band-level misalignment drives electron flow from the polymer to the metal oxide, establishing a Schottky-type heterojunction [13, 14]. This interfacial charge redistribution creates a depletion region, a bottleneck for charge transfer, that becomes exquisitely sensitive to surface-chemical changes induced by gas adsorption [15]. Gas molecules that donate electrons (reducing gases) or withdraw electrons (oxidizing gases) modulate depletion-layer dimensions, producing large, measurable resistance changes amplified far beyond single-component response. Recent literature extensively documents polypyrrole/metal oxide composites for ammonia sensing:

studies have shown 2–4-fold sensitivity enhancements over pristine components and improved humidity robustness. Similarly, polypyrrole/TiO₂ and polypyrrole/SnO₂ systems have demonstrated synergistic performance gains attributed to heterojunction formation and enlarged interfacial contact areas [16, 17].

Despite extensive investigation of polypyrrole/metal oxide composites for ammonia sensing, systematic studies on H₂S detection remain strikingly sparse. Published research on pristine MoO₃ for H₂S sensing is limited; available reports document response magnitudes of 55–70% at 75–150°C but reveal poor selectivity against ammonia and other interferents. Critically, to the best of our knowledge, no published study has systematically investigated polypyrrole/MoO₃ composites specifically for H₂S gas sensing. Existing polypyrrole/MoO₃ literature addresses only ammonia sensing or supercapacitor electrodes, leaving an unexploited research opportunity. This gap is scientifically significant because (1) Mo–S coordination is thermodynamically favorable, molybdenum exhibits strong affinity for chalcogens, making H₂S chemisorption on MoO₃ surfaces more robust than NH₃ physisorption; (2) H₂S and NH₃ exhibit fundamentally different bonding modes with molybdenum sites, enabling selectivity ratios potentially exceeding those observed with other metal-oxide systems; and (3) incorporating the polypyrrole component enables adequate sensitivity without elevated-temperature operation, directly addressing power consumption and safety constraints of conventional sensors.

The present work develops a novel polypyrrole/MoO₃ nanocomposite gas sensor engineered specifically for rapid, highly sensitive, room-temperature H₂S detection. Our investigation systematically examines the synthesis, structural characterization, and gas-sensing performance of this composite material, providing mechanistic insights into heterojunction-enhanced H₂S detection. By integrating polypyrrole's superior room-temperature sensitivity and rapid kinetics with MoO₃'s thermal stability and selective surface chemistry, we demonstrate a substantial performance improvement over both pristine components. This work addresses a genuine literature gap and presents a promising sensing solution for real-time H₂S monitoring in geothermal operations, petrochemical facilities, wastewater treatment plants, and environmental applications.

2. Experimental

2.1. Materials

Molybdenum trioxide (MoO₃) nanopowder (orthorhombic phase, specific surface area ≥ 10 m²/g, particle size 20–50 nm) was obtained from commercial suppliers (Sigma-Aldrich). Pyrrole monomer (C₄H₅N, reagent-grade, 99% purity) was purchased and stored at 4°C. Iron(III) chloride (FeCl₃, anhydrous) and polystyrene sulfonate (PSS, average molecular weight $\sim 70,000$ Da) served as the oxidative polymerization initiator and dopant, respectively. Ultrapure deionized water (Milli-Q system, resistivity ≥ 18.2 M Ω ·cm), absolute ethanol (99.9%, analytical grade), and dichloromethane (analytical grade) were used as solvents. Comb-type copper interdigitated electrode (IDE) substrates were fabricated on printed circuit board (PCB) with dimensions of 1 cm $\times$ 1 cm. The IDE configuration consisted of 12 interdigitated fingers with a width of 0.8 mm, length of 6 mm, and gap spacing of 0.5 mm — 12 fingers of 8 mm cannot

fit a 10 mm substrate to provide enhanced charge collection efficiency and improved electrochemical response characteristics. Test gases, hydrogen sulfide (H_2S), ammonia (NH_3), nitrogen dioxide (NO_2), and carbon monoxide (CO) at 100 ppm certified standards in nitrogen, were obtained from commercial gas suppliers. All reagents were used as received without further purification.

2.2. Preparation of Polypyrrole

Polypyrrole was synthesized via chemical oxidative polymerization using iron(III) chloride as the oxidizing agent [18]. Polystyrene sulfonate (1.0 g) was dissolved in 50 mL ultrapure deionized water by magnetic stirring at room temperature for 2 hours. Freshly distilled pyrrole monomer (0.5 mL) was added dropwise to the PSS solution under continuous stirring. The mixture was cooled to 0–5°C in an ice bath. Iron(III) chloride (1.5 g) dissolved in 20 mL deionized water was added dropwise over 30 minutes, maintaining temperature below 10°C throughout polymerization to control reaction kinetics and prevent degradation. The reaction mixture was stirred for an additional 12 hours at room temperature, during which the solution transitioned from light yellow to deep blue-black, indicating complete polypyrrole formation. The resulting suspension was collected by vacuum filtration through 0.45 μm polyvinylidene fluoride (PVDF) membranes and sequentially washed with deionized water (3×50 mL), ethanol (3×50 mL), and dichloromethane (2×50 mL) to remove unreacted monomers, oligomers, and residual dopant. The black solid was dried under vacuum at 60°C for 8 hours, yielding polypyrrole powder.

2.3. Preparation of Polypyrrole/ MoO_3 Composite

The polypyrrole/ MoO_3 composite was prepared via in-situ polymerization on the MoO_3 surface to establish intimate interfacial contact [19]. Polystyrene sulfonate (0.8 g) and MoO_3 nanopowder (0.5 g) were dispersed in 40 mL deionized water by ultrasonication for 20 minutes at 40 kHz, 200 W using an ultrasonic bath (Elmasonic S30 H, Elma Schmidbauer GmbH, Sauerlach, Germany). Pyrrole monomer (0.4 mL) was added to the suspension, and the mixture was cooled to 0–5°C. Iron(III) chloride (1.2 g dissolved in 15 mL deionized water) was added dropwise over 30 minutes under continuous magnetic stirring at temperatures below 10°C. The reaction proceeded for 12 hours at room temperature with constant stirring. The composite suspension was collected by vacuum filtration and washed using the same protocol as pristine polypyrrole. The dried composite powder was lightly ground in an agate mortar to break aggregates and ensure a free-flowing powder. The polypyrrole/ MoO_3 mass ratio was fixed at 1:1 (w/w) based on preliminary optimization studies, selected to balance electronic properties and maximize interfacial contact between components.

2.4. Electrode Fabrication

For electrode fabrication, copper IDE substrates (1 cm $\times$ 1 cm PCB with 12-finger comb configuration; finger width 0.8 mm, length 6 mm, gap spacing 0.5 mm) were cleaned via sequential ultrasonication in acetone (10 min), ethanol (10 min), and deionized water (10 min), followed by drying at 100°C for 30 minutes to remove organic contaminants and ensure proper surface conditions [20]. Material dispersions were prepared by suspending 10 mg of polypyrrole and Polypyrrole/ MoO_3 composite powder in 1 mL of ethanol, followed by sonication for 10 minutes to achieve a uniform colloidal

dispersion. The dispersion (200 μL) was deposited onto the IDE substrate via drop-casting and dried at 80°C for 2 hours. This deposition–drying cycle was repeated three times to build up film thickness and ensure uniform coating over the interdigitated electrode fingers. The dried composite film was allowed to cure at room temperature for 24 hours prior to gas-sensing measurements.

2.5. Gas Sensor Performance and Setup

A custom-built gas-flow chamber (Teflon, ~ 200 mL internal volume) was employed for chemoresistive gas-sensing measurements. Copper IDE substrates with deposited polypyrrole and polypyrrole/ MoO_3 composite films were placed inside the chamber with electrical leads connected via sealed feedthroughs. Mass-flow controllers (Aalborg, Models GFC-17 and FCST) maintained constant gas flow at 200 mL/min. Real-time electrical resistance was measured using a Keithley 4200A Semiconductor Characterization System (Tektronix Inc., Beaverton, OR, USA) operating in DC resistance mode, with data logged every 2 seconds.

Baseline stabilization was performed in dry air at room temperature ($25 \pm 1^\circ\text{C}$) for 60 minutes. Baseline resistance (R_0) was defined as the average resistance during the final 10 minutes of stabilization when drift was $< 1\%$ per minute. For H_2S sensitivity evaluation, concentrations of 5, 10, 50, 100, 150, 200, and 250 ppm were prepared with dry nitrogen. Gas response was calculated as: $S(\%) = [(R_g - R_0) / R_0] \times 100$, where R_0 is baseline resistance and R_g is steady-state resistance at plateau. Response time (t_{90}) and recovery time (t_{rec}) were extracted from resistance–time curves as the times to reach 90% of the total resistance change on exposure and on recovery respectively [21].

3. Results and discussion

3.1. Crystalline Structure and Phase Composition

Figure 1. XRD patterns of pure polypyrrole, MoO_3 and the polypyrrole/ MoO_3 composite.

X-ray diffraction patterns, as shown in Fig. 1, reveal distinct structural signatures for each material component. Pure polypyrrole exhibits a broad, featureless diffraction hump centered near $2\theta = 20^\circ$, characteristic of amorphous conducting polymers lacking long-range crystalline order [22]. In contrast, pure MoO_3 displays sharp, well-defined diffraction peaks consistent with the orthorhombic crystal structure (space group Pbnm), matching JCPDS file 47-1081 (Molybdenum Oxide, MoO_3 , orthorhombic). The principal peaks at $2\theta \approx 12.6^\circ$ (020), 25.7° (040), and 38.2° (021) correspond to the crystallographic planes characteristic of this phase, with additional reflections at $2\theta \approx 49.2^\circ$ (060) and 62.4° (080) visible at higher angles [23]. The polypyrrole/ MoO_3 composite XRD pattern superimposes the crystalline MoO_3 peaks with the broad amorphous hump from polypyrrole, indicating successful integration of both phases while preserving the orthorhombic MoO_3 crystallinity. The absence of new diffraction peaks at intermediate angles confirms that no secondary phases, impurities, or molybdenum oxide hydrates (such as $\text{MoO}_3 \cdot \text{H}_2\text{O}$ or intermediate oxides such as MoO_2) were formed during composite synthesis, validating the physical blending strategy and the absence of chemical reactions between polypyrrole and

MoO₃. This phase purity is critical for gas-sensing performance, as MoO₃ crystallinity is directly linked to surface reactivity, oxygen-vacancy density, and charge-carrier mobility.

3.2. Vibrational Spectroscopy and Interfacial Interactions

Figure 2. FTIR spectra of pure polypyrrole, MoO₃ and the polypyrrole/MoO₃ composite.

Fourier-transform infrared spectroscopy, as illustrated in Fig. 2, characterizes the molecular structure and interfacial interactions in the polypyrrole/MoO₃ composite. Pure polypyrrole exhibits characteristic conducting-polymer vibrations: a sharp, strong absorption at 1550 cm⁻¹ assigned to N–H in-plane bending coupled with aromatic C = N stretching of the pyrrole ring, diagnostic of the p-doped polypyrrole backbone. The 1300–1500 cm⁻¹ envelope shows two distinct peaks corresponding to quinoid (C = N⁺) and benzenoid (C = C) ring modes, confirming the partially oxidized state expected for PSS-doped polypyrrole. Secondary absorptions at ~ 1000–1200 cm⁻¹ represent C–N stretching [24].

Pure MoO₃ displays a dramatically simpler spectrum dominated by a single, intense, sharply-defined absorption peak at approximately 1000 cm⁻¹, assigned to Mo = O terminal stretching vibrations characteristic of the orthorhombic crystal structure. A broad absorption centered near 3300 cm⁻¹ reflects surface-adsorbed hydroxyl groups and moisture, typical for metal-oxide nanopowders. The polypyrrole/MoO₃ composite spectrum shows all polypyrrole modes (1550, 1400, 1300, 1000–1200, 700–800 cm⁻¹) preserved, confirming phase coexistence without covalent bonding [25]. The composite exhibits two diagnostic modifications of MoO₃: (1) peak broadening and (2) intensity reduction of the Mo = O stretch at 1000 cm. These selective changes, without new absorption bands, are diagnostic of interfacial charge transfer. Electron transfer from polypyrrole to MoO₃ weakens the terminal Mo = O bond (Mo⁶⁺ → Mo⁵⁺), weakening the Mo = O bond (peak broadening) and decreasing oscillator strength (intensity loss).

3.3. Optical Properties and Charge-Transfer Characteristics

Figure 3. UV–vis absorbance spectra of pure polypyrrole, MoO₃ and the polypyrrole/MoO₃ composite.

UV-visible absorbance spectroscopy, as presented in Fig. 3, demonstrates synergistic optical properties and evidence of heterojunction-induced charge-transfer transitions in the polypyrrole/MoO₃ composite. Pure polypyrrole exhibits strong, broad absorbance across the entire wavelength range (200–900nm), with a prominent absorption peak at ~ 210–220 nm and sustained elevated absorbance extending to longer wavelengths. This strong, broad absorption is characteristic of conducting polymers with extensive electronic conjugation and polaron/bipolaron charge carriers, reflecting the extended π -electron system of the p-doped polypyrrole backbone. The high absorbance magnitude throughout the visible region indicates efficient light absorption across multiple energy states [26].

Pure MoO₃ displays distinctly lower absorbance magnitude compared to polypyrrole, with a sharp absorption peak at the shortest wavelengths (~ 210 nm) and a relatively flat, low-absorbance baseline

extending to longer wavelengths. This spectral profile is consistent with the well-defined optical bandgap of orthorhombic MoO_3 (~ 2.8 eV); the sharp absorption edge represents electronic transitions from the valence band to the conduction band, while the low absorbance at longer wavelengths (lower energies) reflects the absence of transitions below the bandgap [27]. The polypyrrole/ MoO_3 composite displays intermediate absorbance with enhanced visible-region absorbance (200–900 nm) compared to pure MoO_3 , indicating synergistic charge-transfer transitions at the polymer–oxide interface. The band offset between p-type polypyrrole and n-type MoO_3 creates interfacial CT transitions that generate additional visible-region absorbance. This CT absorption enhances photo-generated charge-carrier density and interfacial charge-transfer kinetics, supporting the improved gas-sensing sensitivity.

3.4. Surface Morphology

Figure 4. FE-SEM images of (a) pure polypyrrole and (b) the polypyrrole/ MoO_3 composite. Scale bars 5 μm .

Field-emission scanning electron microscopy, as presented in Fig. 4, reveals the morphological transformation accompanying composite formation. Pure polypyrrole, as shown in Fig. 4a, exhibits the characteristic cauliflower-like globular morphology typical of chemically oxidative-polymerized pyrrole, consisting of near-spherical primary grains of approximately 200–500 nm that aggregate into larger interconnected clusters of 2–5 μm [16]. The uniform grain size distribution indicates homogeneous nucleation during polymerization, while the loosely packed cluster arrangement generates an open, three-dimensional porous network with abundant inter-particle voids. This porosity is advantageous for gas sensing as it provides accessible diffusion channels and a high density of surface adsorption sites, although the intrinsically low conductivity of the polymer limits the translation of surface events into measurable resistance changes.

The polypyrrole/ MoO_3 composite, as shown in Fig. 4b, displays a markedly different hierarchical architecture. Large, well-faceted MoO_3 microplates with smooth surfaces, sharp edges and lateral dimensions of 2–6 μm dominate the field of view, consistent with the layered orthorhombic structure confirmed by XRD. These plates are decorated with the fine granular polypyrrole phase, which is no longer present as the continuous dense network observed in Fig. 4a but is instead distributed as discrete sub-micron aggregates anchored on the oxide surfaces. A representative elongated MoO_3 belt in the central region is conformally covered by a dense layer of polypyrrole granules, providing direct visual evidence that polymerization nucleated preferentially at the oxide surface rather than in bulk solution. Regions of exposed, uncoated MoO_3 remain visible, indicating partial rather than complete encapsulation, which is favourable for sensing because both the oxide surface and the polymer–oxide boundary remain accessible to the analyte [28].

3.5. Current–Voltage Characteristics and Charge-Transport Behaviour

Figure 5. Current–voltage characteristics over ± 2 V on copper interdigitated electrodes for (a) pure polypyrrole and (b) the polypyrrole/ MoO_3 composite.

Two-probe I–V measurements were carried out on copper interdigitated electrodes over a ± 2 V window at room temperature in dry air, as shown in Fig. 5. Pure polypyrrole shows a symmetric but clearly non-linear characteristic, the current rising from ± 3.9 μA at ± 1 V to ± 9.2 μA at ± 2 V. The chord resistance at 2 V is ~ 217 k Ω , while the differential resistance near zero bias is higher at ~ 290 k Ω , decreasing to ~ 180 k Ω at maximum bias. This progressive fall in differential resistance with increasing field is characteristic of barrier-limited hopping transport and is consistent with the granular morphology seen by FE-SEM, in which conduction proceeds by carrier hopping across contact points between loosely packed polymer grains.

The polypyrrole/MoO₃ composite, as presented in Fig. 5b, exhibits a fundamentally different regime: the characteristic is strictly linear through the origin, giving an ohmic resistance of ~ 1.05 k Ω from a current of ± 1.90 mA at ± 2 V. The composite is therefore ~ 206 times more conductive than the pristine polymer, with the field-dependent behaviour entirely suppressed. Both curves are symmetric about the origin, confirming ohmic, non-injecting copper contacts and establishing that the non-linearity in pure polypyrrole originates in the bulk transport pathway rather than at the electrodes.

This enhancement is attributed to interfacial charge transfer between the two phases. MoO₃ possesses a deep work function and high electron affinity, and on intimate contact, accepts electrons from the polypyrrole backbone, generating a high density of free holes in the polymer while weakening the terminal Mo = O bond. The same process has been reported for in-situ polymerised polypyrrole/MoO₃ composites and for MoO₃-loaded polypyrrole derivatives, where charge transfer between polymer and oxide phases enhances electrical performance and narrows the optical band gap [29, 30]. It is independently evidenced here by the broadening of the Mo = O band in FTIR. The elevated hole density narrows the inter-grain barriers sufficiently for carriers to tunnel rather than hop, converting the transport from field-activated hopping to ohmic conduction. Practically, the low baseline resistance improves signal-to-noise in the sensing measurement, while the retained p-type character means H₂S, as an electron donor, compensates these holes and raises the resistance, consistent with the response behaviour reported.

3.6. Gas-Sensing Performance

Figure 6. Dynamic response to 5–250 ppm H₂S at room temperature: (a) pure polypyrrole, (b) polypyrrole/MoO₃ composite, and (c, d) two further composite sensors demonstrating reproducibility.

The amplitude of the resistive response and the associated adsorption–desorption kinetics are the two parameters against which a chemiresistive device is principally judged. The sign of the resistance change is determined jointly by the redox character of the analyte and by the identity of the majority carrier within the sensing film [29]. Hydrogen sulfide is a reducing species that donates electron density upon adsorption; in a p-type material, where holes constitute the majority carriers, this donated charge compensates a fraction of the hole population and the film resistance therefore rises. Both pristine polypyrrole and the polypyrrole/MoO₃ composite behave in exactly this manner, confirming that hole transport governs conduction in each case and that the oxide, although an n-type semiconductor in

isolation, does not invert the carrier polarity of the composite. It is worth distinguishing this pathway from the protonation mechanism frequently invoked for polyaniline-based H_2S sensors, in which the weakly acidic analyte protonates imine nitrogens and thereby increases conductivity [31]. The pyrrole nitrogen is a considerably poorer proton acceptor than the polyaniline imine, so that route is largely unavailable here, and the observed resistance increase confirms that electron donation and hole compensation dominate the transduction.

Figure 6 (a and b) presents the dynamic response of the two sensors to seven consecutive H_2S pulses spanning 5 to 250 ppm at room temperature. In both materials, the resistance rises sharply upon admission of the analyte, reaches a plateau, and returns towards its original baseline once the chamber is purged with dry air, establishing that the interaction is fully reversible under ambient conditions without any thermal regeneration. The response amplitude increases monotonically with concentration throughout the interval examined. Pristine polypyrrole rises from approximately 20% at 5 ppm to 68% at 250 ppm, whereas the composite increases from roughly 45% to 205% across the same interval, corresponding to an enhancement factor of 2.1 to 3.0 at every concentration tested. Significantly, this margin widens with increasing concentration, which indicates that the composite possesses a substantially larger reservoir of accessible adsorption sites rather than merely transducing the same surface chemistry more efficiently.

The concentration dependence of both sensors departs from strict proportionality, rising steeply at low concentrations before flattening appreciably towards the upper end of the range. This profile is characteristic of Langmuir-type adsorption onto a finite population of surface sites: at low partial pressure, essentially every incident molecule encounters a vacant site, whereas progressive site occupancy limits further uptake at higher concentrations. The saturation is far more pronounced in the pristine polymer, which gains only fourteen percentage points between 50 and 250 ppm, compared with eighty-seven percentage points for the composite over the identical interval. This contrast constitutes the clearest evidence in the dataset that MoO_3 introduces additional, chemically distinct adsorption centres, the coordinatively unsaturated molybdenum surface sites and oxygen vacancies, which supplement rather than simply modify the adsorption capacity of the polymer. Over the range 100 to 250 ppm, the composite response remains closely linear, which is the interval of greatest practical relevance for occupational monitoring, where the OSHA ceiling limit lies.

Device-to-device reproducibility was assessed by fabricating two additional composite sensors under nominally identical conditions and subjecting them to the same concentration sequence, as shown in Fig. 6 (c and d). Both devices reproduce the response magnitudes and transient profiles of the original sensor across the full range, confirming that the synthesis and deposition protocol yields films of consistent performance. Such consistency is a prerequisite for any scaled fabrication and is frequently omitted from reports of composite sensing materials.

Response and recovery kinetics were evaluated at 100 ppm, as presented in Fig. 7(a and b). The pristine polymer exhibits a response time of 107 s and a recovery time of 85 s, whereas the composite responds

in 88 s and recovers in 58 s. The composite is therefore some 18% faster in response and 32% faster in recovery, with the larger improvement appearing in the desorption half of the cycle. Two factors account for this acceleration, both independently evidenced elsewhere in this work. The I–V characteristics establish that the composite is two orders of magnitude more conductive than the pristine polymer, so that the carrier redistribution following a surface perturbation equilibrates correspondingly faster. Additionally, the hierarchical architecture revealed by FE-SEM, in which polypyrrole granules decorate micron-scale MoO₃ platelets, presents a more open and accessible pore structure than the densely agglomerated cauliflower morphology of the pristine polymer, permitting more rapid gas diffusion into and out of the film. In both materials, the recovery time is shorter than the response time, which indicates that adsorption is predominantly physisorptive or weakly chemisorptive in character and desorbs readily at ambient temperature, a favourable attribute, since strongly chemisorbed analytes typically require thermal regeneration and yield protracted recovery. These kinetics compare favourably with room-temperature polymer/oxide H₂S sensors reported recently, for which response and recovery times in the range 78–88 s are typical.

Figure 7. Sensing characteristics at 100 ppm H₂S: response and recovery transients of (a) pure polypyrrole and (b) the composite; (c) selectivity against interfering gases; (d) stability over 60 days.

Selectivity was examined against ammonia, nitrogen dioxide, ethanol and carbon monoxide, each at 100 ppm, the same concentration as the H₂S reference, as illustrated in Fig. 7c. The composite responds at 133% to H₂S, 55% to NH₃, 35% to NO₂, 20% to ethanol and 12% to CO, yielding selectivity coefficients of 2.4, 3.8, 6.7 and 11.1, respectively. Ammonia is the most significant interferent, which is expected, since it dedopes polypyrrole directly through nitrogen lone-pair donation without needing to reach the oxide phase. The discrimination in favour of H₂S originates in the thermodynamic preference of molybdenum for sulfur: the soft-acid character of the molybdenum surface centre pairs favourably with the soft-base sulfur donor, producing a Mo–S interaction substantially stronger than the dative nitrogen coordination available to ammonia or the weak physisorption available to ethanol and carbon monoxide. Carbon monoxide gives the smallest response, consistent with its requiring elevated temperature for meaningful activation on either phase. The pattern across the interferent series, therefore, tracks the expected hierarchy of binding strength and supports the proposed Mo–S coordination mechanism.

Long-term stability was monitored over sixty days, the sensor being re-tested at 100 ppm every five days following full baseline re-stabilisation in dry air, as shown in Fig. 7d. The response declined gradually from 133% initially to 116% at day sixty, corresponding to 87.2% retention of the original sensitivity; at the thirty-day mark, the retention was 94.7%. The decline is slow and approximately linear rather than exhibiting any abrupt degradation, and the modest scatter about the trend, amounting to a few percentage points between successive measurements, reflects ordinary measurement reproducibility rather than systematic drift. The residual loss is attributable to slow dedoping and partial overoxidation of the polypyrrole backbone under ambient storage, together with a contribution from surface species not completely desorbed at room temperature between exposures. That approximately seven-eighths of the initial response survives two months of intermittent operation reflects the stabilising role of the oxide

phase, which both shields the polymer from atmospheric oxidation and sustains a charge-transfer doping that, unlike conventional small-molecule dopants, cannot be lost by leaching [32]. A recently reported In_2O_3 –PANI composite of comparable 1:1 composition achieved a maximum response of 84.2% at 25°C, against 44.9% for the pristine polymer [32]; the polypyrrole/ MoO_3 system described here delivers 133% at 100 ppm and 205% at 250 ppm, with the same p-type transduction signature and without any requirement for heating.

A comparison with recently reported H_2S sensors places the present material favourably within the ambient-temperature class that now dominates this field, almost all such devices having abandoned the heated metal-oxide platforms that once required operation at 200°C or above [33]. Among systems that quantify response as a relative resistance change in percentage terms, the polypyrrole/ MoO_3 composite delivers 133% at 100 ppm and 205% at 250 ppm, exceeding the 98.98% obtained at 70 ppm from a CdS@PPy/rGO ternary composite [34] and the 84.24% reported for an In_2O_3 –PANI composite of comparable 1:1 stoichiometry [32], the latter being a particularly close analogue in that it likewise couples a p-type conducting polymer to an n-type oxide and likewise exhibits a resistance increase upon exposure. This performance is achieved without noble-metal catalysts, photoactivation or ternary additives, the enhancement arising solely from interfacial charge transfer between the two constituent phases. The response and recovery times of 88 s and 58 s are shorter than those of several comparable polymer–oxide systems [6, 34], although nanostructured architectures with shorter diffusion paths achieve faster kinetics at lower concentrations [35]; notably, recovery here is faster than response, indicating weak chemisorption that reverses spontaneously and requires no thermal regeneration. The most substantial advantage lies in durability, with 87.2% of the initial response retained after sixty days of intermittent operation, a longer ageing assessment than the forty-nine-to-fifty-four-day studies reported elsewhere, and in a working range of 5–250 ppm that spans the full occupational-exposure regime [6, 34, 36, 37].

Overall, the sensing data establish the polypyrrole/ MoO_3 composite as a room-temperature H_2S sensor in which every performance metric traces back to a single structural cause. The 2.1- to 3.0-fold gain in response over the pristine polymer, the accelerated response and recovery kinetics, the preferential affinity for sulfur over the competing analytes, and the retention of 87.2% of the initial sensitivity after two months of intermittent operation all follow from the interfacial charge transfer that the current–voltage and FTIR measurements independently identify – XRD shows the absence of reaction and FE-SEM shows morphology; neither evidences charge transfer. The oxide does not merely dilute or template the polymer; it dopes it, supplies catalytically active molybdenum surface sites, and shields it from the ambient oxidation that ordinarily limits the working life of conducting-polymer sensors. That this combination is achieved without heating, noble-metal catalysts or additional components is what recommends it for deployment in the environments where H_2S exposure constitutes a practical hazard.

Conclusion

A polypyrrole/MoO₃ nanocomposite prepared by in-situ oxidative polymerisation functions as a sensitive, selective and durable room-temperature H₂S sensor. The two phases coexist without chemical reaction, yet their contact transforms the electronic behaviour: selective perturbation of the terminal Mo = O vibration, and a 206-fold conductivity increase accompanied by a transition from hopping to ohmic transport establishes that MoO₃ p-dopes the polymer rather than acting as an inert filler. This single mechanism accounts for the sensing behaviour. The composite responds with a resistance increase characteristic of hole-dominated conduction, reaching 133% at 100 ppm and 205% at 250 ppm, two to three times the pristine polymer, with response and recovery times of 88 and 58 s. Selectivity against ammonia, nitrogen dioxide, ethanol and carbon monoxide confirms that discrimination originates in Mo–S coordination, and 87.2% of the initial response survives sixty days. Operating without heating, catalysts or additives, the material offers a practical route to low-power H₂S monitoring; humidity tolerance remains to be established.

Declarations

Author Contribution

M.N.M. is the sole author of this manuscript. M.N.M. conceived and designed the study, synthesised the polypyrrole and polypyrrole/MoO₃ materials, fabricated the sensor devices, performed all structural, spectroscopic and electrical characterisation, carried out the gas-sensing measurements, analysed and interpreted the data, prepared all figures, and wrote and reviewed the manuscript.

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Figures

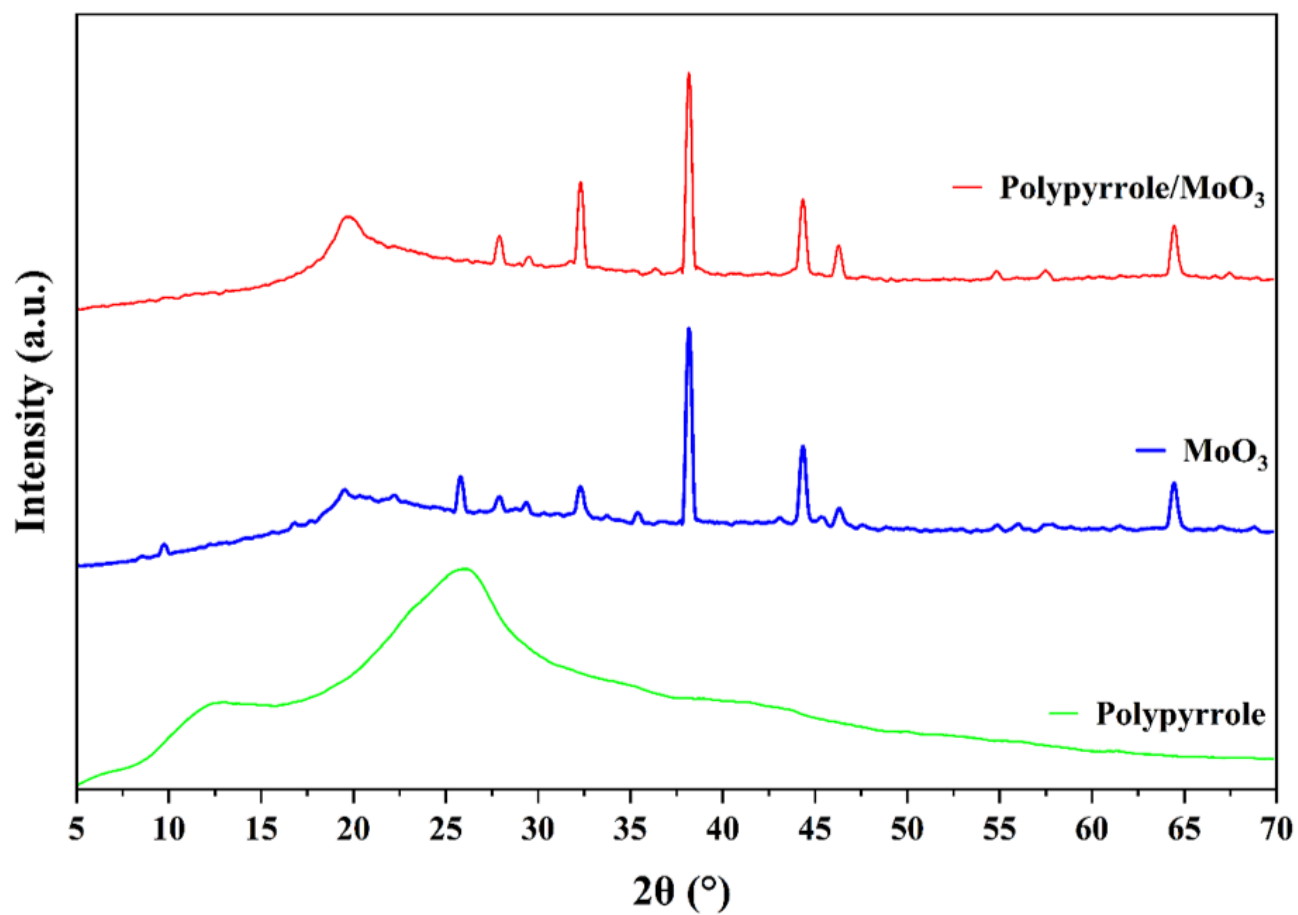


Figure 1

XRD patterns of pure polypyrrole, MoO₃ and the polypyrrole/MoO₃ composite.

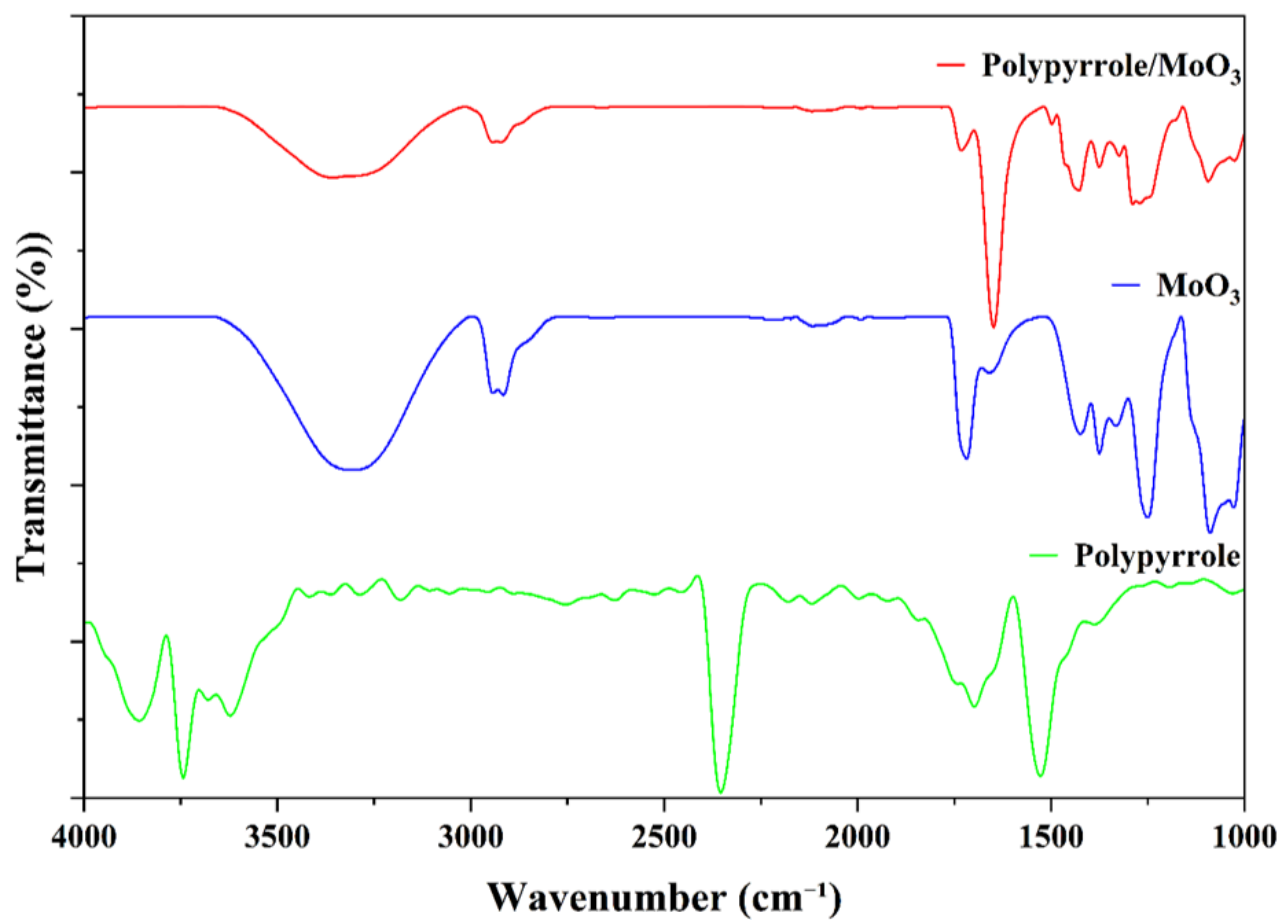


Figure 2

FTIR spectra of pure polypyrrole, MoO₃ and the polypyrrole/MoO₃ composite.

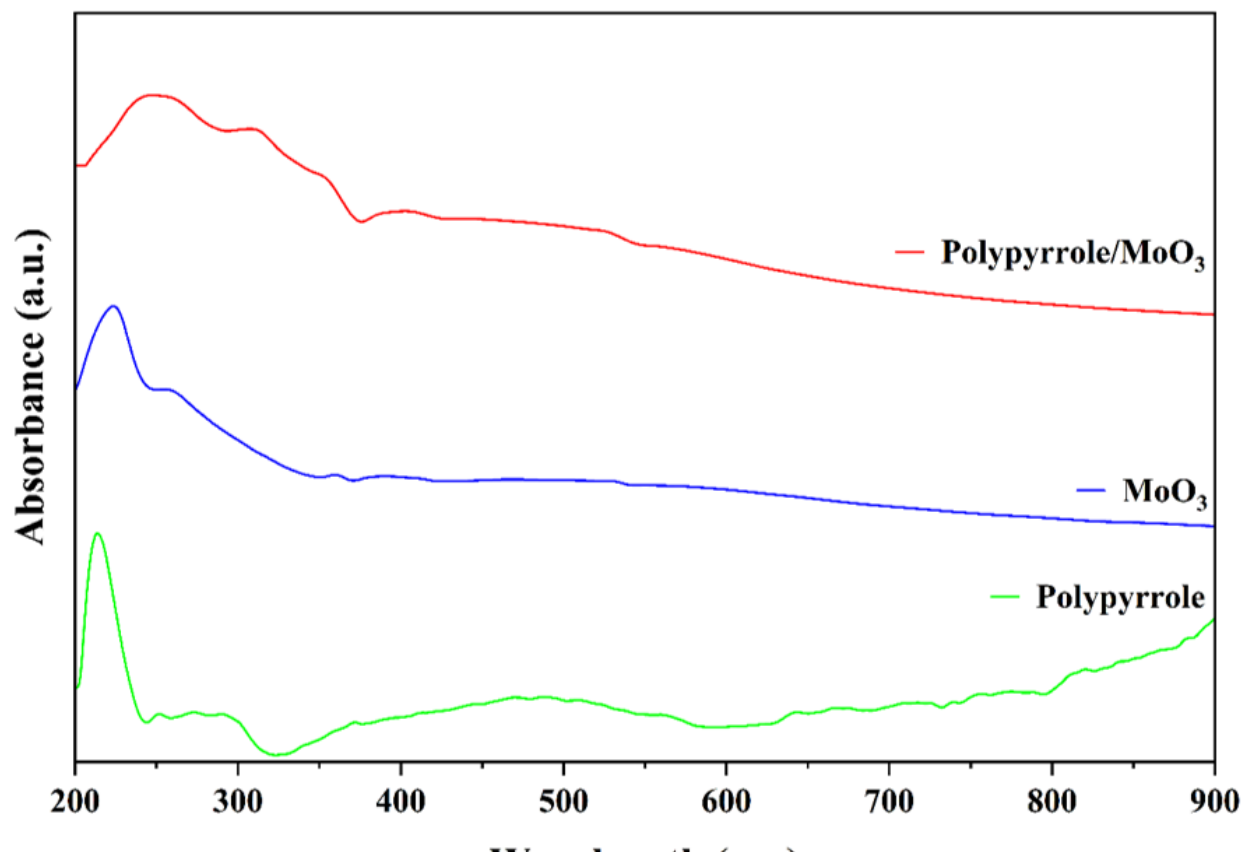


Figure 3

UV-vis absorbance spectra of pure polypyrrole, MoO₃ and the polypyrrole/MoO₃ composite.

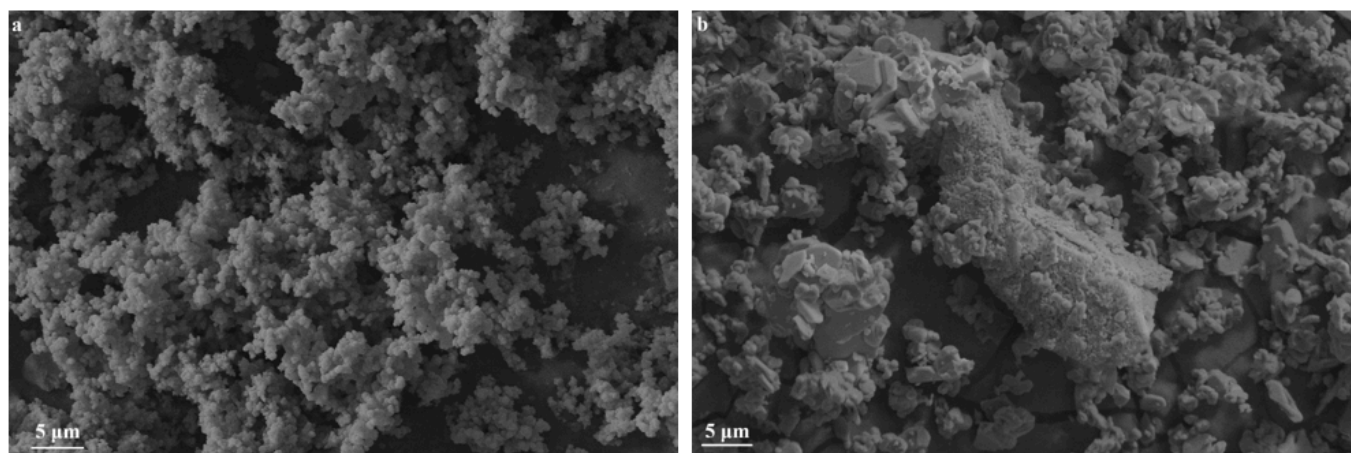


Figure 4

FE-SEM images of (a) pure polypyrrole and (b) the polypyrrole/MoO₃ composite. Scale bars 5 μm.

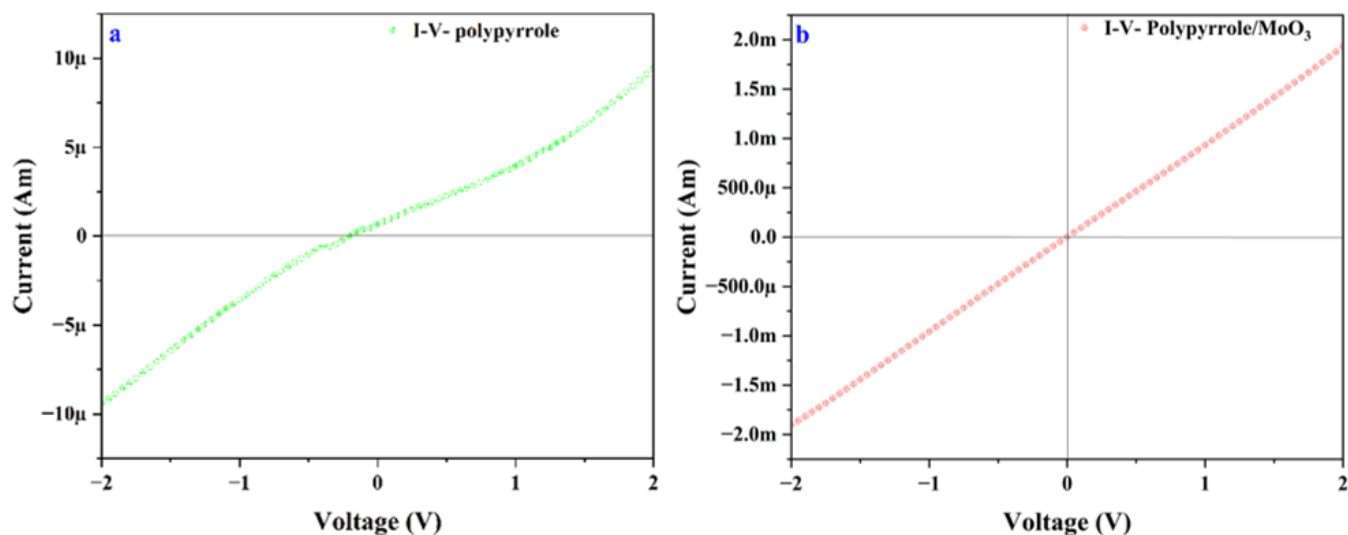


Figure 5

Current–voltage characteristics over ± 2 V on copper interdigitated electrodes for (a) pure polypyrrole and (b) the polypyrrole/MoO₃ composite.

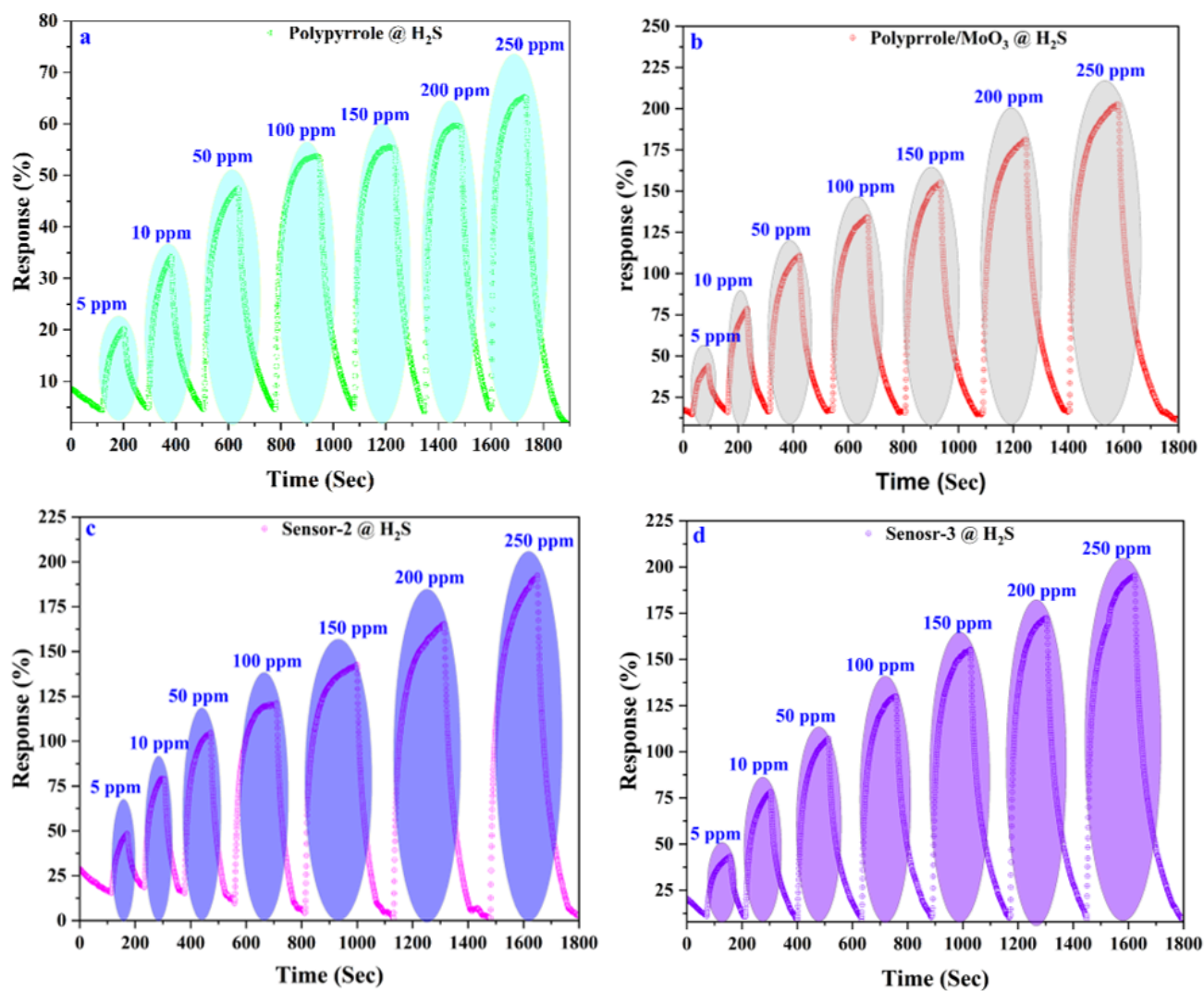


Figure 6

Dynamic response to 5–250 ppm H₂S at room temperature: (a) pure polypyrrole, (b) polypyrrole/MoO₃ composite, and (c, d) two further composite sensors demonstrating reproducibility.

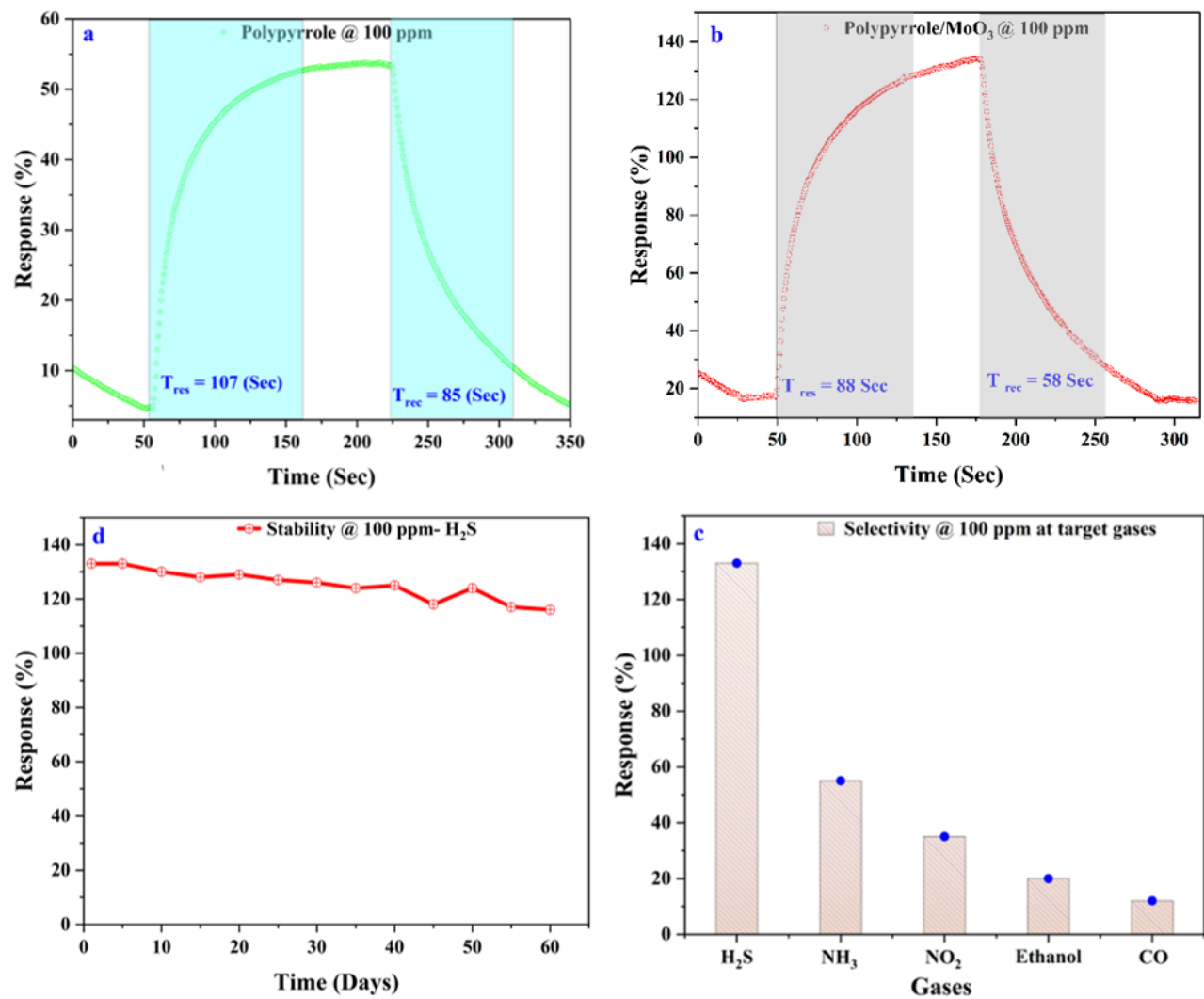


Figure 7

Sensing characteristics at 100 ppm H₂S: response and recovery transients of (a) pure polypyrrole and (b) the composite; (c) selectivity against interfering gases; (d) stability over 60 days.