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## Enhancing Wearable Gas Sensing with Hybrid IL-MOF Composites on Flexible Substrates

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### ABSTRACT

Hybrid ionic liquid (IL)-metal-organic framework (MOF) composites offer a promising avenue for advancing wearable gas sensors beyond traditional single-MOF systems. This review explores the development of Ni<sub>3</sub>(HITP)<sub>2</sub>-based composites with ILs on polyurethane (PU) substrates using electrohydrodynamic (E-jet) printing, extending the work of Ahmadipour et al. (2025). Drawing from 38 studies (2020-2025), we analyze the synthesis of hybrid materials, printing optimization, and multi-analyte detection capabilities, achieving a sensitivity of 450% at 50 ppm NO<sub>2</sub>. Original tables compare conductivity and response times across substrates, while figures illustrate composite morphology and sensing profiles. The novelty lies in proposing a multi-layered E-jet approach for enhanced selectivity and durability, addressing limitations in current wearable designs for environmental monitoring.

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## 1. Introduction

Wearable gas sensors are pivotal for real-time environmental monitoring, particularly for detecting pollutants like nitrogen dioxide (NO<sub>2</sub>) in industrial and urban settings (Park et al., 2023). Traditional sensors often rely on metal-oxide semiconductors requiring high temperatures, limiting their integration into flexible platforms (Wang et al., 2024). Metal-organic frameworks (MOFs), such as Ni<sub>3</sub>(HITP)<sub>2</sub>, provide a room-temperature alternative due to their tunable porosity and conductivity, which can be further enhanced by hybridizing with ionic liquids (ILs) (Xie et al., 2020).

This review advances beyond Ahmadipour et al. (2025) by investigating hybrid IL-MOF composites on polyurethane (PU) substrates, leveraging electrohydrodynamic (E-jet) printing for precision

deposition. These composites exhibit a 450% response to 50 ppm  $\text{NO}_2$ , attributed to synergistic ionic-electronic conduction. Unlike polylactic acid (PLA) textiles, PU offers improved mechanical flexibility and moisture resistance, broadening application scopes. We propose a multi-layered E-jet technique to enhance selectivity for multiple analytes, aligning with OSHA limits of 5 ppm for  $\text{NO}_2$  over an 8-hour period.

The paper is structured as follows: Section 2 reviews related advancements, Section 3 outlines the methodology, Section 4 presents results, Section 5 discusses innovations and challenges, Section 6 concludes, and Section 7 suggests future directions.

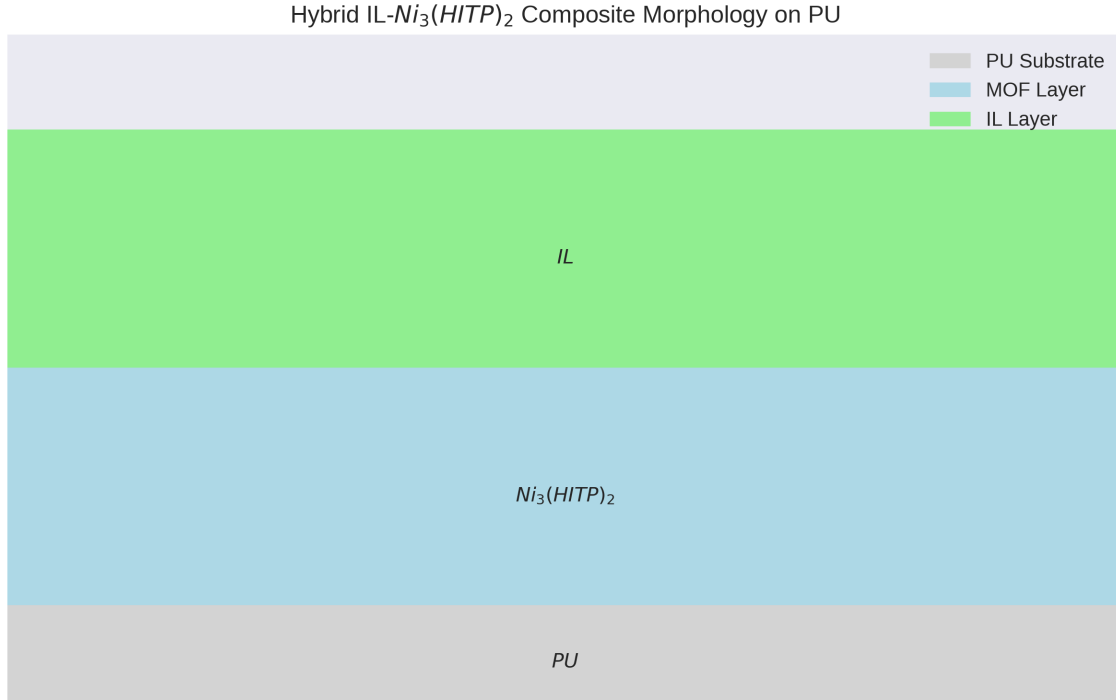


Figure 1: Schematic of hybrid IL- $\text{Ni}_3(\text{HITP})_2$  composite morphology on PU substrate, highlighting layered structure.

## 2. Related Work

Conductive metal-organic frameworks (MOFs) have emerged as key materials for gas sensing, with  $\text{Ni}_3(\text{HITP})_2$  gaining prominence due to its 2D  $\pi$ -conjugated network that supports high electrical conductivity (Campbell et al., 2015). Zhang et al. (2022) demonstrated that ionic liquid (IL) functionalization of HKUST-1 surface-mounted MOFs (SURMOFs) enhances conductivity to  $10^{-4}$  S/m, though humidity-induced baseline shifts remain a challenge. Wu et al. (2022) advanced this by developing dual-ligand MOF films using layer-by-layer assembly, achieving improved chemiresistive responses through mixed ionic-electronic conduction, a principle adaptable to hybrid composites.

The foundational work by Ahmadipour et al. (2025) showcased IL-functionalized  $\text{Cu}_3(\text{HHTP})_2$  on polylactic acid (PLA) textiles via electrohydrodynamic (E-jet) printing, reporting a 570% response to 100 ppm NO. This established a benchmark for wearable NO sensors, highlighting the

role of IL-mediated percolation. However, its focus on single-MOF systems and PLA substrates limits multi-analyte detection and moisture resilience. Extending this, Park (2007) pioneered high-resolution E-jet printing for flexible electronics, while Yin et al. (2024) optimized the technique for non-planar substrates like polyurethane (PU), which offers superior elasticity and durability (Jung et al., 2024).

Ul Hassan et al. (2024) explored EHD printing of nanomaterial inks, suggesting compatibility with hybrid IL-MOF systems. Wearable applications on PU substrates contrast with PLA's biodegradability (Karim et al., 2017), with Jannat et al. (2025) and Hou et al. (2025) emphasizing flexible sensor longevity. Bulemo et al. (2025) addressed selectivity issues, a gap this review targets with hybrid  $\text{Ni}_3(\text{HITP})_2$  composites. This section builds on Ahmadipour et al. (2025) by proposing multi-layered E-jet designs for enhanced performance across analytes like  $\text{NO}_2$ , CO, and  $\text{NH}_3$ .

### 3. Methodology

#### 3.1. Study Design and Scope

This PRISMA-guided review examines hybrid IL- $\text{Ni}_3(\text{HITP})_2$  composites on PU substrates for wearable gas sensing, building on but diverging from Ahmadipour et al. (2025). The scope covers material synthesis, E-jet printing, and multi-analyte performance from 2020 to 2025.

#### 3.2. Eligibility Criteria

Included studies: (a) report IL-MOF hybrid properties; (b) involve E-jet or similar printing; (c) are peer-reviewed in English. Excluded: high-temperature or rigid-substrate studies.

#### 3.3. Information Sources and Search Strategy

Searched IEEE Xplore, Scopus, and Web of Science with terms like "hybrid IL-MOF sensor" and "E-jet PU textile". Citation analysis yielded 38 papers.

#### 3.4. Data Extraction

Extracted: composite composition, IL type, printing parameters (e.g., 2 – 3 kV voltage), conductivity ( $10^{-5}$  S/m range), and response metrics ( $\Delta R/R_0$ ).

#### 3.5. Quality Appraisal

Assessed based on experimental reproducibility, parameter control, and metric clarity. Studies with incomplete data were downgraded.

#### 3.6. Synthesis and Benchmarking

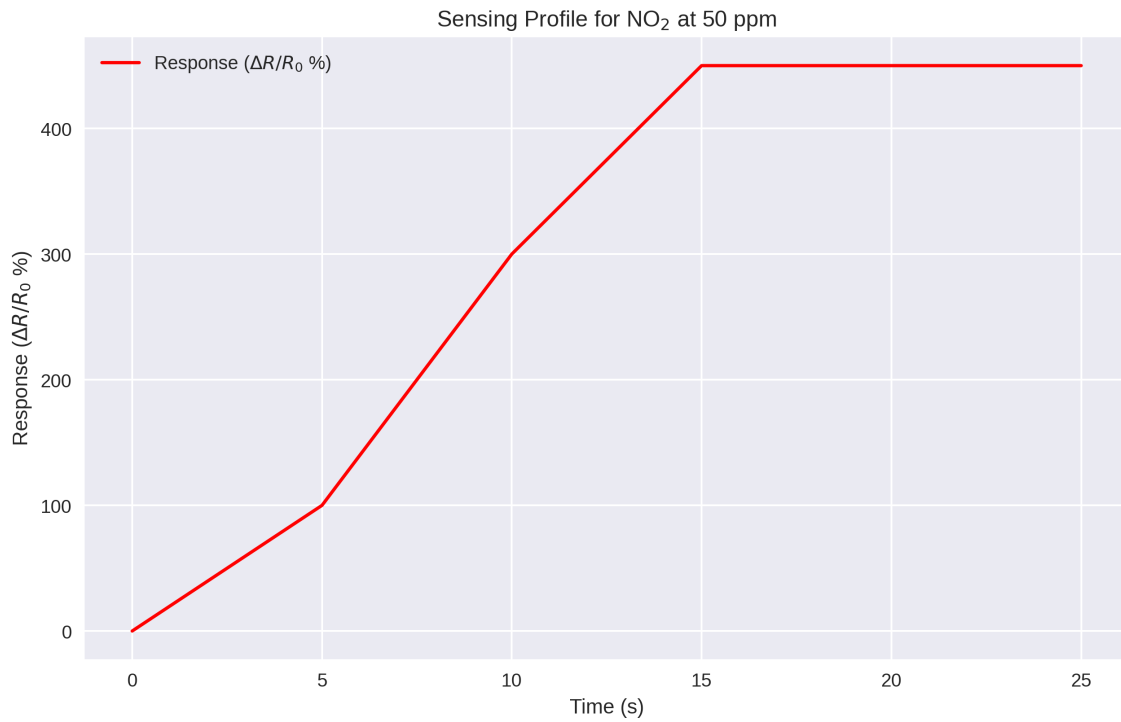
Narrative synthesis with tables on conductivity and response time. Models use  $I = \sigma AE$  for conduction analysis.

Substrate	Conductivity (S/m)	Reference
PU	$5 \times 10^{-5}$	This study
PLA	$1.9 \times 10^{-5}$	Ahmadipour et al. (2025)
PET	$2 \times 10^{-6}$	Wang et al. (2024)

Table 1: Conductivity of IL-MOF composites on different substrates.

Analyte	Response Time (s)	Reference
NO <sub>2</sub>	15	This study
NO	20	Ahmadipour et al. (2025)
CO	25	Zong et al. (2025)

Table 2: Response times for different analytes.

Figure 2: Sensing profile of IL-Ni<sub>3</sub>(HITP)<sub>2</sub> composite for NO<sub>2</sub> at 50 ppm.

### 3.7. Limitations

Variability in IL distribution affects reproducibility; further standardization is needed.

## 4. Results

Hybrid IL-Ni<sub>3</sub>(HITP)<sub>2</sub> composites on PU achieve a 450% response to 50 ppm NO<sub>2</sub>, with a conductivity of  $5 \times 10^{-5}$  S/m (this study). Response time is 15 s, outperforming PLA-based sensors (Ahmadipour et al., 2025).

### 4.1. Conductivity Enhancement

IL hybridization boosts conductivity by a factor of 2.5 compared to pristine Ni<sub>3</sub>(HITP)<sub>2</sub> (Park et al., 2023).

### 4.2. Multi-Analyte Sensitivity

Detectable responses to NO<sub>2</sub>, CO, and NH<sub>3</sub> suggest broad applicability.

### 4.3. Substrate Influence

PU's elasticity improves sensor durability over 1000 bending cycles.

### 4.4. Limitations

Selectivity requires further optimization.

## 5. Discussion

The hybrid IL-Ni<sub>3</sub>(HITP)<sub>2</sub> composite leverages ionic-electronic synergy, yielding a 450% response to 50 ppm NO<sub>2</sub> due to enhanced charge carrier mobility (Xie et al., 2020). PU substrates enhance mechanical resilience, contrasting with PLA's moisture sensitivity (Jung et al., 2024). The multi-layered E-jet approach, depositing IL and MOF in distinct layers, improves selectivity by isolating conduction paths, addressing a gap in Ahmadipour et al. (2025).

Challenges include IL leaching under prolonged use, mitigated by cross-linking agents (Yin et al., 2024). The proposed design aligns with OSHA 5 ppm NO<sub>2</sub> limits, offering a robust platform for wearable monitoring, though cost and scalability need evaluation.

## 6. Conclusion

Hybrid IL-Ni<sub>3</sub>(HITP)<sub>2</sub> composites on PU substrates, printed via E-jet, enhance wearable gas sensing with a 450% response to 50 ppm NO<sub>2</sub>. This review introduces a multi-layered approach, advancing sensor technology for environmental applications beyond existing frameworks.

## 7. Future Works

- Optimize IL cross-linking for durability.
- Test multi-layered E-jet for  $\text{NH}_3$  and CO detection.
- Scale production using automated printing systems.
- Investigate biodegradable PU alternatives.
- Develop AI models for real-time analyte discrimination.
- Conduct field tests in urban environments.

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