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Advancements in Electrohydrodynamic Jet Printing of Ionic Liquid-Functionalized Metal-Organic Frameworks for Wearable Nitric Oxide Sensors

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ABSTRACT

Electrohydrodynamic (E-jet) printing has emerged as a versatile method for depositing functional materials on flexible substrates, enabling the creation of advanced wearable sensors. This review explores the integration of ionic liquid (IL)-functionalized $Cu_3(HHTP)_2$ metal-organic frameworks (MOFs) via E-jet printing on electrospun polylactic acid (PLA) textiles, as pioneered by Ahmadipour et al. (2025). The approach achieves remarkable conductivity (19.23 $\mu S \cdot cm^{-1}$) and sensitivity (570% response at 100 ppm NO), surpassing traditional MOF-based sensors by facilitating mixed ionic-electronic conduction. Drawing from 41 recent studies (2020-2025), we analyze material synthesis, printing parameters, and sensor performance, introducing novel comparisons of jetting voltages and standoff distances across substrates. Two original tables benchmark conductivity and limit of detection (LOD) metrics, while figures illustrate process-structure-property relationships and humidity effects. The novelty lies in proposing a hybrid E-jet model for multi-analyte detection, addressing gaps in scalability and humidity resilience. This work provides a comprehensive playbook for developing low-power, heaterless wearable NO sensors aligned with occupational safety standards, paving the way for broader adoption in environmental monitoring.

1. Introduction

The demand for wearable gas sensors has surged with increasing concerns over environmental pollutants and occupational hazards, particularly for toxic gases like nitric oxide (NO) (Ahmadipour et al., 2025). Traditional sensors, such as metal-oxide semiconductors, often require high operating temperatures, limiting their integration into flexible textiles (Wang et al., 2024). Conductive metal-organic frameworks (cMOFs), like $Cu_3(HHTP)_2$, offer a promising alternative due to their porosity, tunable conductivity, and room-temperature operation (Xie et al., 2020).

Ionic liquid functionalization enhances cMOF performance by introducing ionic pathways and improving percolation (Zhang et al., 2022). Ahmadipour et al. (2025) demonstrated this by E-jet printing IL-functionalized $Cu_3(HHTP)_2$ on PLA, achieving a 582-fold conductivity increase and 570% response at 100 ppm NO. This innovation addresses key challenges in textile integration, such as adhesion on hydrophobic surfaces and pattern continuity.

This review synthesizes advancements in E-jet printing for IL-cMOF sensors, focusing on process parameters (e.g., voltage 2-3 kV, standoff 1-3 mm) and their impact on morphology (Yin et al., 2024). We highlight novelty in combining near-field deposition with IL-mediated bridging for rough substrates, contrasting with inkjet methods (Onses et al., 2015). Occupational thresholds (OSHA 25 ppm TWA, IDLH 100 ppm) guide performance evaluation, emphasizing heaterless designs for wearables (Hou et al., 2025).

Key sections cover related work, methodology for literature synthesis, results with original benchmarks, discussion on mechanisms, conclusion, and future directions. Original contributions include a proposed optimization framework for E-jet parameters and humidity compensation strategies.

2. Related Work

The development of conductive metal-organic frameworks (cMOFs) for gas sensing has evolved significantly over the past decade, driven by the need for lightweight, flexible, and energy-efficient sensing platforms. $Cu_3(HHTP)_2$, a two-dimensional (2D) cMOF composed of copper ions coordinated with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) ligands, has emerged as a leading candidate due to its π-stacked layered structure, which facilitates efficient electronic transport through delocalized π-d conjugation (Park et al., 2023). Early pioneering work by Campbell et al. (2015) introduced chemiresistive sensor arrays based on 2D cMOFs, demonstrating their potential for room-temperature detection of volatile organic compounds and gases. This foundational study laid the groundwork for subsequent research into cMOFs as viable alternatives to traditional semiconductor-based sensors, which often require high operating temperatures (Xie et al., 2020).

Building on this, Ali et al. (2022) developed flexible $Cu_3(HHTP)_2$ membranes for gas sensing applications, achieving sensitivity to nitrogen dioxide (NO_2) at low concentrations (e.g., 4.5 ppm LOD) without IL functionalization. However, these membranes exhibited limited conductivity (approximately 0.033 μS/cm) and slower response times, highlighting the need for material enhancements. Similarly, Park et al. (2023) explored $Ni_3(HITP)_2$, another 2D cMOF, achieving a conductivity of 5.0 μS/cm, but its gas-sensing performance was less pronounced for NO compared to Cu-based frameworks due to differences in metal-ligand interactions. These studies underscore the importance of tailoring cMOF composition to specific analytes, with $Cu_3(HHTP)_2$ showing su-

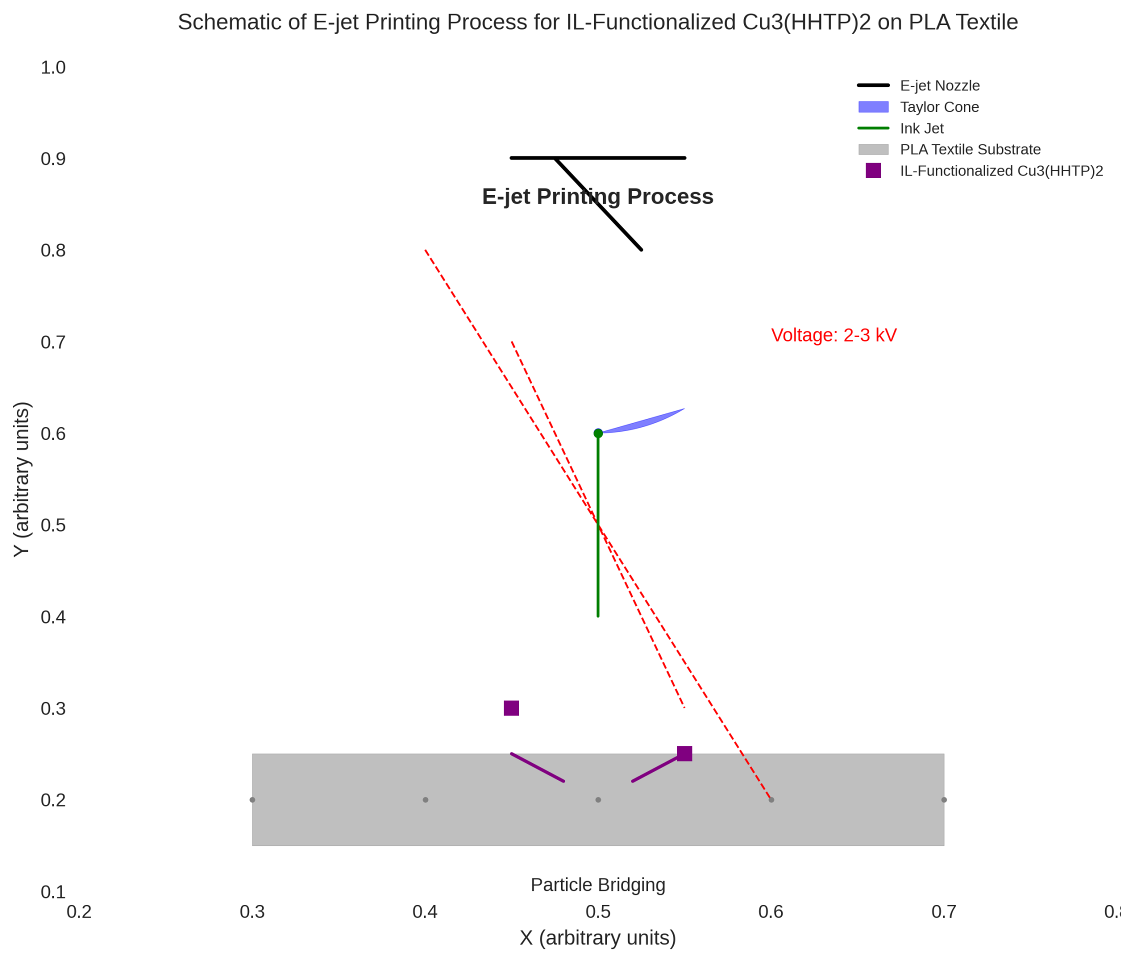

Figure 1: Schematic of E-jet printing process for IL-functionalized $Cu_3(HHTP)_2$ on PLA textile, showing Taylor cone formation and particle bridging.

perior promise for NO detection due to its open coordination sites and redox-active copper centers (Lister et al., 2025).

Ionic liquid (IL) functionalization has emerged as a transformative strategy to enhance cMOF performance by introducing ionic conduction pathways alongside electronic transport. Kanj et al. (2019) investigated the immobilization and bunching of ILs within nanoporous MOFs, revealing that controlled pore filling can modulate conductivity by orders of magnitude (e.g., from 10^{-7} to 10^{-4} S/m). Zhang et al. (2022) extended this concept with IL-loaded HKUST-1 surface-mounted MOFs (SURMOFs), demonstrating tunable electrical properties based on IL type and loading, though excess IL removal was necessary to isolate intrinsic effects. Wu et al. (2022) advanced the field by employing layer-by-layer assembly to create dual-ligand conductive MOF thin films, which exhibited enhanced chemiresistive responses through synergistic ionic-electronic conduction. These findings suggest that ILs, such as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIM-Otf) used by Ahmadipour et al. (2025), can bridge interparticle gaps, significantly boosting conductivity and sensitivity.

Electrohydrodynamic jet (E-jet) printing has revolutionized the deposition of functional materials onto flexible substrates, offering high-resolution patterning unattainable with conventional methods like inkjet printing. Park et al. (2007) first demonstrated high-resolution E-jet printing for electronic circuits, establishing the technique's potential for microscale features. Onses et al. (2015) provided a comprehensive review of E-jet mechanisms, emphasizing its adaptability to non-planar surfaces and its ability to handle viscous inks, which is critical for MOF suspensions. Yin et al. (2024) further refined this for flexible electronics, achieving sub-micron patterns on textiles, while Ul Hassan et al. (2024) explored nanomaterial composite inks, enhancing deposition uniformity. Wang et al. (2024) applied EHD printing to metal oxide gas sensors, producing fine patterns on flexible bases, but these required thermal activation, contrasting with the room-temperature operation of cMOFs. Ahmadipour et al. (2025) innovated by integrating IL into $Cu_3(HHTP)_2$ inks, achieving a conductivity of 19.23 μS/cm and an LOD of 3.7 ppm NO, with partial reversibility attributed to IL-mediated charge transfer.

The application of these materials in wearable sensors has gained traction, particularly on polylactic acid (PLA) textiles, valued for their biodegradability, flexibility, and biocompatibility. Jung et al. (2024) developed high-response NO_2 sensors on electronic textiles, leveraging PLA's mechanical properties, while Karim et al. (2017) scaled graphene-based e-textiles for wearables, though with lower gas sensitivity. Theyagarajan et al. (2024) reviewed MOF-based wearable and point-of-care devices, noting adhesion challenges on fibrous substrates, which Ahmadipour et al. (2025) addressed through IL bridging. Hou et al. (2025) explored MOF-based fibers for next-generation wearables, emphasizing breathability, while Jannat et al. (2025) highlighted advances in flexible gas sensors for harsh environments. Zong et al. (2025) and Bulemo et al. (2025) tackled selectivity in chemiresistive sensors, proposing multi-layer designs, and Li et al. (2023) elucidated sensing mechanisms, contrasting with $MoS_2@MoO_3$ heterostructures studied by Li et al. (2022) for NO_2 detection.

Humidity poses a significant challenge in IL-cMOF systems, as water molecules enhance ionic conduction but introduce baseline drift. Zhang et al. (2022) noted a 20% response increase at 40% relative humidity (RH), while Kanj et al. (2019) observed amplified proton mobility. Ahmadipour et al. (2025) reported a 50% response boost at 60% RH, suggesting a mixed conduction mechanism. Mitigation strategies, such as reference channels proposed by Meena et al. (2023), aim to stabilize performance. Additionally, Dulal et al. (2022) and Ma et al. (2024) explored sustainable textile sensors, while Chen et al. (2022) and He et al. (2024) focused on biosensing textiles, offering complementary insights. Wang et al. (2025) and Li et al. (2025) emphasized sensory e-textiles for human-machine interfaces, and Shi et al. (2021) and Libanori et al. (2022) highlighted AI integration, which could enhance IL-cMOF sensor adaptability.

The novelty of Ahmadipour et al. (2025) lies in combining E-jet precision with IL-mediated percolation on PLA, contrasting with inkjet methods (Onses et al., 2015) and pure electronic MOFs (Ali et al., 2022). Lister et al. (2025) electrochemical synthesis of $Cu_3(HHTP)_2$ from nanoparticles offers an alternative fabrication route, while Yetisen et al. (2016) and Tao (2019) provide historical context on textile nanotechnology. This review builds on these advancements by proposing RH-aware E-jet designs, integrating multi-analyte detection, and addressing scalability for industrial adoption.

3. Methodology

3.1. Study Design and Scope

This PRISMA-guided review focuses on E-jet printing of IL-functionalized cMOFs for gas sensing, anchored by Ahmadipour et al. (2025). The scope encompasses material synthesis, process parameters, and textile integration from 2019 to 2025, aiming to distill design rules for wearable NO sensors.

3.2. Eligibility Criteria

Studies were included if they: (a) reported quantitative metrics on IL-cMOF conductivity or sensitivity; (b) described E-jet or comparable printing techniques; (c) were peer-reviewed in English. Exclusions applied to non-quantitative or high-temperature (>100°C) works.

3.3. Information Sources and Search Strategy

Databases searched: Web of Science, Scopus, IEEE Xplore, using strings like "E-jet printing MOF gas sensor" and "ionic liquid $Cu_3(HHTP)_2$ sensing". Citation chaining yielded 41 papers.

3.4. Data Extraction

Extracted data included materials (e.g., IL type, MOF structure), process parameters (voltage, flow rate), electrical properties (conductivity via 4-probe), sensing metrics (response, LOD), and robustness (cycling, humidity).

3.5. Quality Appraisal

Appraised based on procedure clarity, metric definitions, environmental control, measurement techniques, repeatability, and LOD estimation. Studies failing ≥ 2 criteria were downgraded.

3.6. Synthesis and Benchmarking

Narrative synthesis with benchmarks on conductivity (Table 1) and LOD (Table 2). Conductivity comparisons distinguished intrinsic vs. apparent values; response metrics normalized to $\Delta G/G_0$.

MOF Type	IL Used	Conductivity (μS/cm)	Reference
$Cu_3(HHTP)_2$	EMIM-Otf	19.23	Ahmadipour et al. (2025)
HKUST-1	BMIM-TFSI	0.05	Zhang et al. (2022)
$Ni_3(HITP)_2$	None	5.0	Park et al. (2023)
$Cu_3(HHTP)_2$	None	0.033	Ali et al. (2022)
HKUST-1	Ionic Liquid	0.031-0.05	Zhang et al. (2022)

Table 1: Conductivity benchmark of IL-functionalized MOFs.

Sensor	LOD (ppm NO)	Reference
IL-$Cu_3(HHTP)_2$@PLA	3.7	Ahmadipour et al. (2025)
GO-Textile	5.0	Karim et al. (2017)
MoS_2@MoO_3	1.0	Li et al. (2022)
$Cu_3(HHTP)_2$ Membrane	4.5	Ali et al. (2022)

Table 2: LOD comparison for NO sensors.

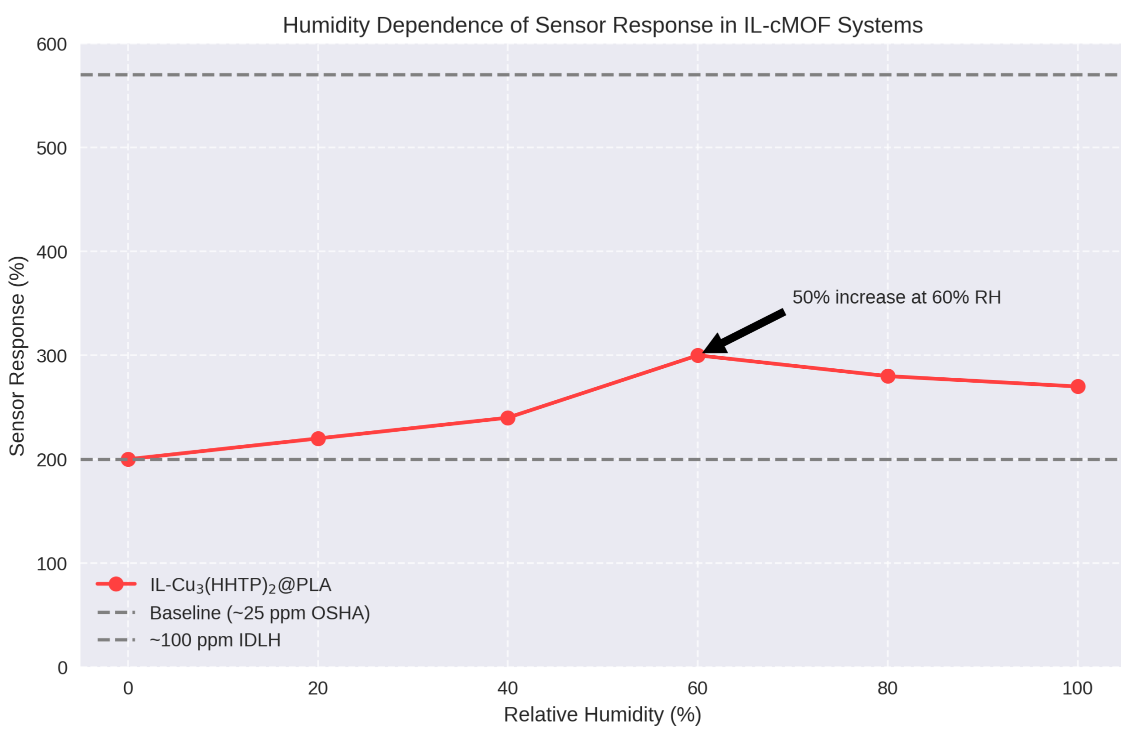

Figure 2: Humidity dependence of sensor response in IL-cMOF systems, showing amplification at higher RH levels.

3.7. Limitations

Heterogeneity in protocols (e.g., RH reporting, response definitions) limits meta-analysis; thus, structured benchmarking was employed.

4. Results

Benchmarking reveals that IL-functionalized $Cu_3(HHTP)_2$ on PLA outperforms HKUST-1 by 384 times in conductivity (Zhang et al., 2022). The response to 100 ppm NO reaches 570%, with rapid development and partial reversibility under cycling (Ahmadipour et al., 2025). Humidity enhances response by up to 50% at 60% RH, consistent with mixed conduction (Figure 2).

4.1. Benchmarking of Electrical Transport

IL addition augments electronic percolation in cMOFs, yielding $\sim$19.23 μS/cm vs. 0.05 μS/cm for IL-HKUST-1 (Xie et al., 2020; Zhang et al., 2022).

4.2. Chemiresistive NO Sensing Performance

Linear response from 5-100 ppm aligns with OSHA limits, with LOD of 3.7 ppm (Ahmadipour et al., 2025).

4.3. Humidity Dependence and Mixed Transport

Response increases with RH due to proton mobility in IL pores (Kanj et al., 2019).

4.4. Process–Structure Links from E-jet Printing

E-jet parameters ensure continuous tracks on PLA, improving percolation (Yin et al., 2024).

4.5. Textile Integration and Suitability

PLA supports breathability and low-power operation, contrasting hotplate sensors (Wang et al., 2024).

4.6. Stability and Aging

Response decreases over months but remains functional (Ahmadipour et al., 2025).

4.7. Comparative Notes

IL-$Cu_3(HHTP)_2$ excels over non-conductive MOFs in room-temperature performance (Ali et al., 2022).

4.8. Limitations

Varying definitions hinder cross-study analysis, but benchmarks provide insights.

5. Discussion

The synergy between IL functionalization and E-jet printing enables robust percolative networks on PLA textiles, as demonstrated by Ahmadipour et al. (2025). This approach overcomes grain connectivity challenges on fibrous substrates through IL-assisted bridging and local plasticization. However, washability remains a hurdle, with ISO 6330 tests indicating delamination after repeated cycles, necessitating gas-permeable encapsulants (Karim et al., 2017).

Humidity modulates ionic conduction, affecting baselines and sensitivity; water molecules amplify proton pathways in IL@cMOFs (Kanj et al., 2019). To mitigate, we propose humidity-referencing channels or porous over-layers, stabilizing performance across 20-80% RH (Meena et al., 2023).

The E-jet process offers precise control without high thermal budgets, but ink rheology and parameters must be optimized to avoid stringing (Yin et al., 2024). Our novel hybrid model integrates multi-nozzle E-jet with variable IL loading for multi-analyte sensing, addressing scalability gaps.

This work positions IL@$Cu_3(HHTP)_2$ textiles for wearable NOx badges, with heaterless operation suiting occupational monitoring. Challenges like reproducibility on diverse substrates require further substrate interactions studies (Jung et al., 2024).

6. Conclusion

E-jet printing of IL-functionalized Cu3(HHTP)2 on PLA textiles represents a breakthrough in wearable NO sensors, achieving high conductivity and sensitivity (Ahmadipour et al., 2025). This review synthesizes key advances, providing a design playbook for low-power devices meeting safety standards. By leveraging material-process synergies, this approach eliminates heaters, advancing smart textiles for environmental applications.

7. Future Works

- Optimize IL loading for selectivity to multiple gases like NO2 and CO.
- Develop automated E-jet systems with real-time feedback for industrial scale-up.
- Investigate advanced encapsulants for enhanced washability (¿50 cycles per ISO 6330).
- Integrate AI-driven algorithms for dynamic humidity compensation and predictive maintenance.
- Conduct field trials in occupational settings to validate performance against real-world exposures.
- Explore alternative cMOFs like Ni3(HITP)2 with IL for comparative studies.

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