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Mixed Metal MOF-on-MOF Sensors for Enhanced Electrical NO_2 Detection

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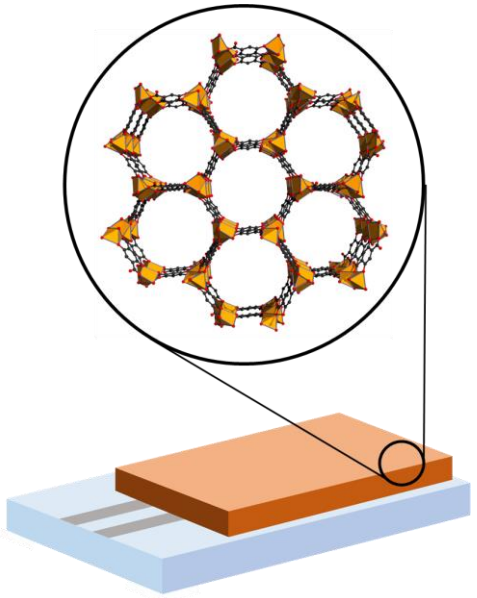
Toxic Gas Detection Requires Improvement of Nanoporous-Based Electrical Sensors

- Acid gases such as NO_x and SO_x pose serious health and safety concerns
- Commercial gas sensors have limitations with power, lifetime, chemical fouling, and/or selectivity
- M-MOF-74 (M = Ni, Mg, Co) shows promise as a nanoporous sorbent for low-power impedance sensors of acid gases

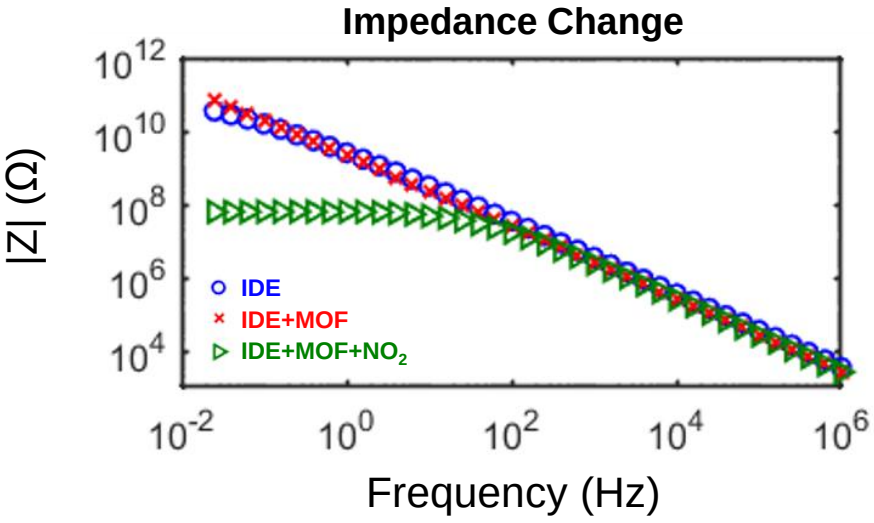
MOF-Based Sensor Operating Principle

InterDigitated Electrode (IDE)



MOF-IDE Sensor

+ Trace Toxic Gas (NO_2)

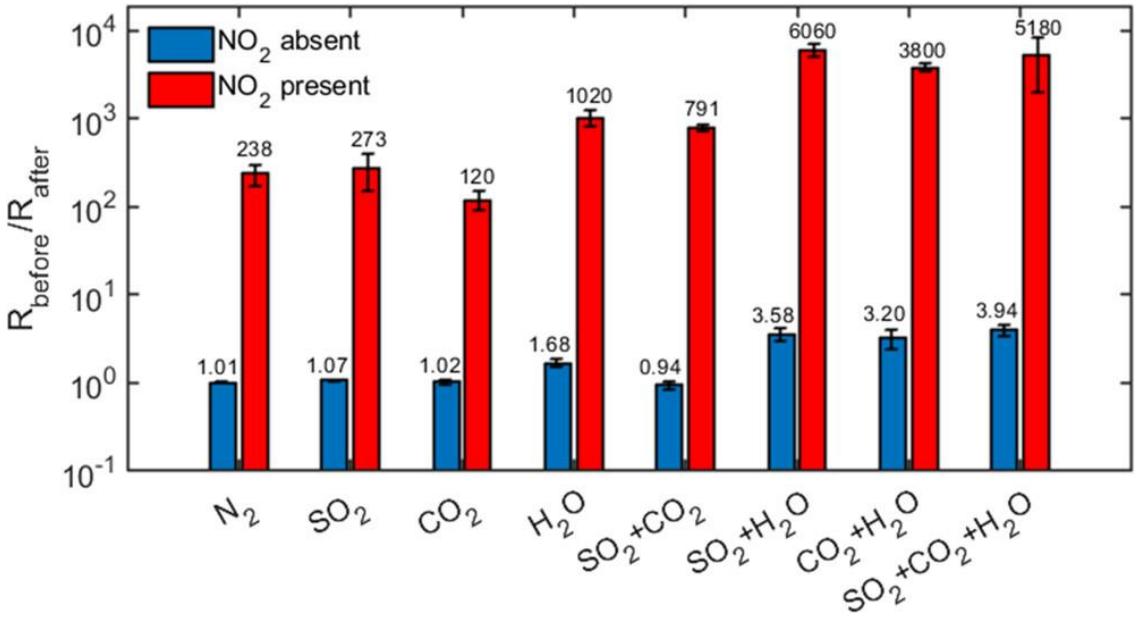


US Patent No. 11,573,217. Feb. 7, 2023.
US CIP Patent No. 18/103,617. Jan. 31, 2023.
US Appl. No. 63/450,260. Mar 6, 2023.

MOF-74-based sensors can reliably detect trace NO_2 gas

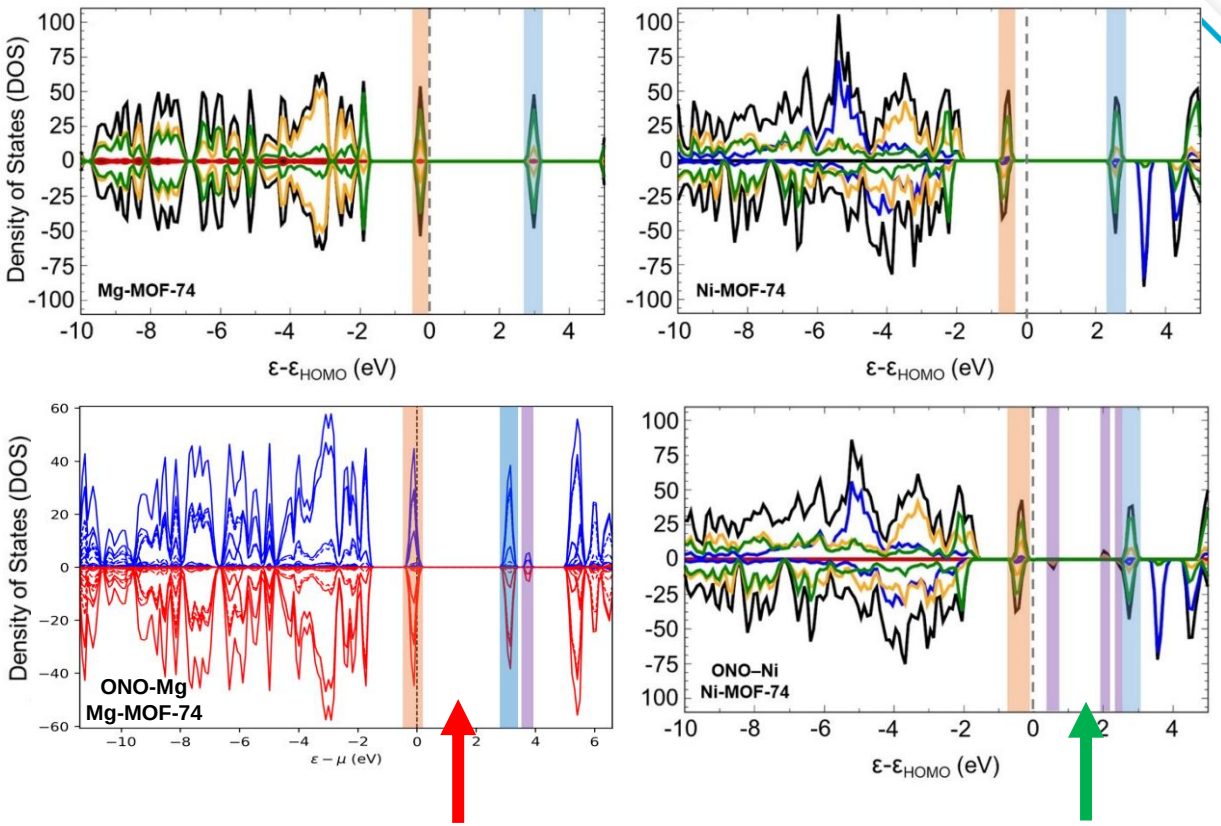
Ni-MOF-74-Based Sensors Show Large Impedance Change in Complex Environments

ACS Appl. Mater. Interfaces **2023**, *15*, 31, 37675–37686



- Ni-MOF-74 selectively detects NO_2 in mixtures of SO_2, CO_2, and H_2O
- Larger impedance change of Ni-MOF-74 upon trace NO_2 exposure due to formation of new states within band gap

Both Mg- and Ni-MOF74 had similar sized band gaps



No new states within band gap of Mg-MOF-74

New States within band gap of Ni-MOF-74

Formation of new states within band gap of Ni-MOF-74 upon NO_2 exposure led to order of magnitude change in impedance

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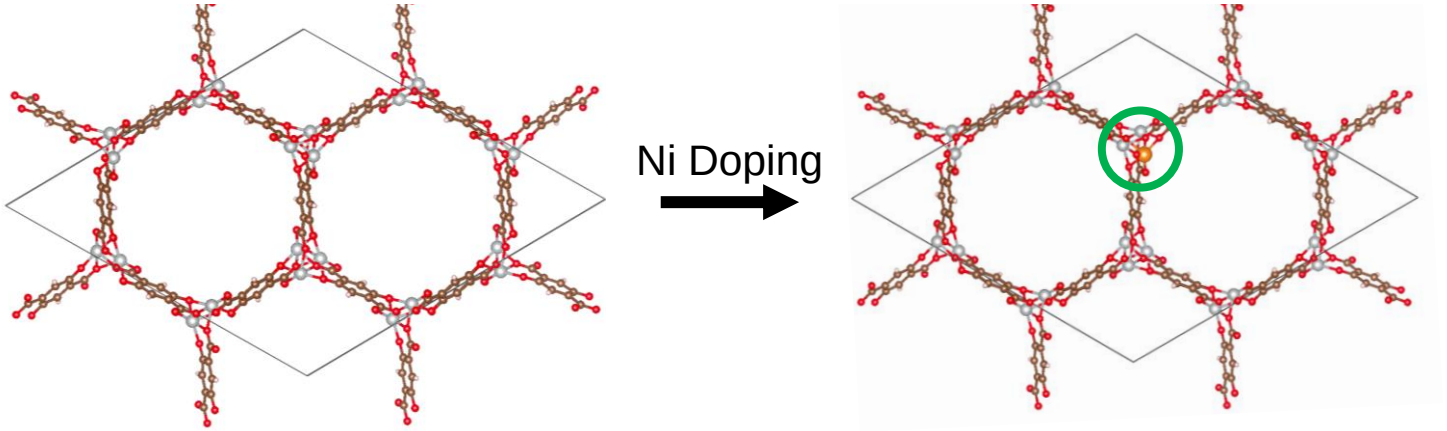
Long-Term Sensor Stability Counter to Framework Stabilities of Mg- and Ni-MOF-74

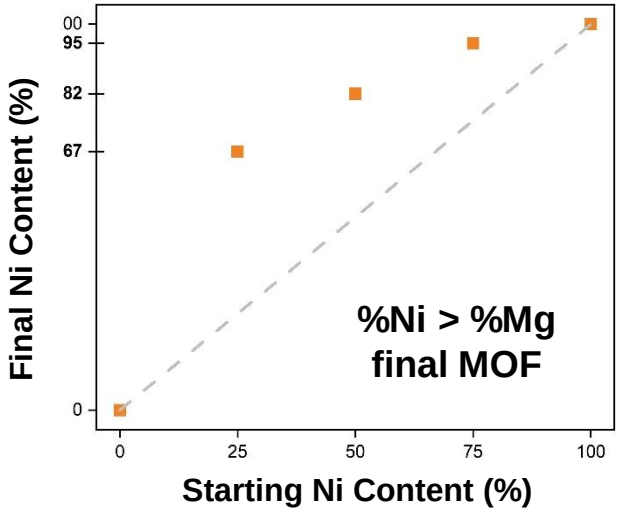
Simulated Doping of Ni in Mg-MOF-74 Showed Increased Framework Stability



Mg-MOF-74 | **$Ni_{0.06}Mg_{0.94}$-MOF-74**

- Both computation and experimental results showed greater stability of Ni-MOF-74
- Ni-MOF-74-based sensors showed ***larger response decreases*** over time, compared to Mg-MOF-74 sensors
- Strong interaction of NO_2 with Ni in MOF-74 likely cause of faster degradation

Experimental Ni Content



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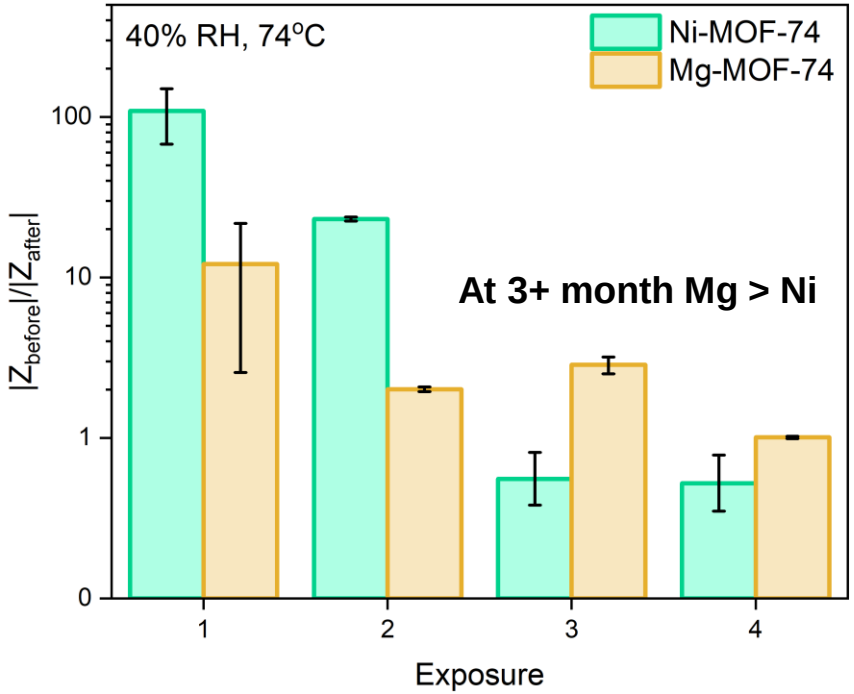
Impedance Change of MOF-74 Sensors Over 4 months

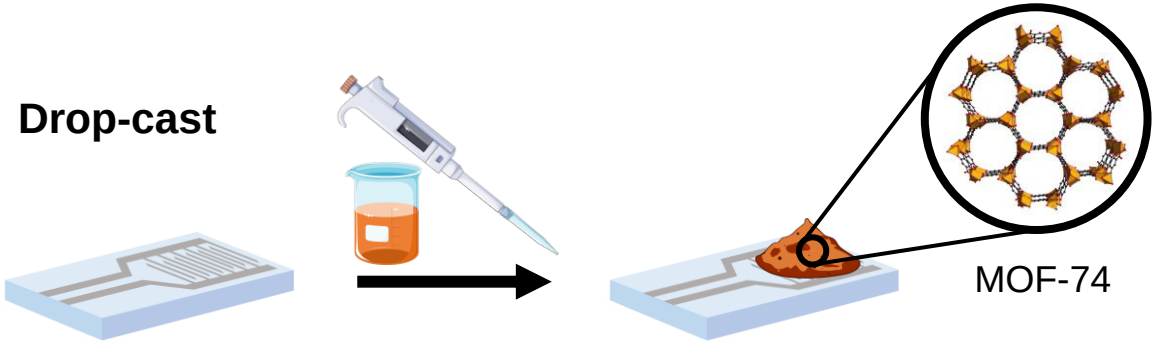


Ind. Eng. Chem. Res. **2023**, *62*, 5, 2336–2345

Metal mixing of Ni and Mg may allow for improved stability without sacrificing sensor performance

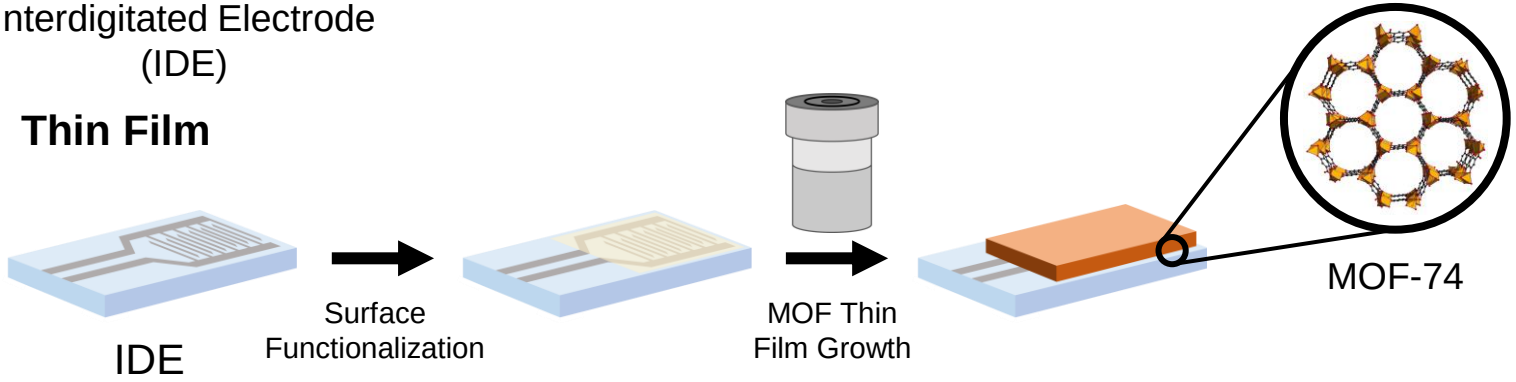
Methods for MOF Thin Film Sensor Synthesis

Drop-cast



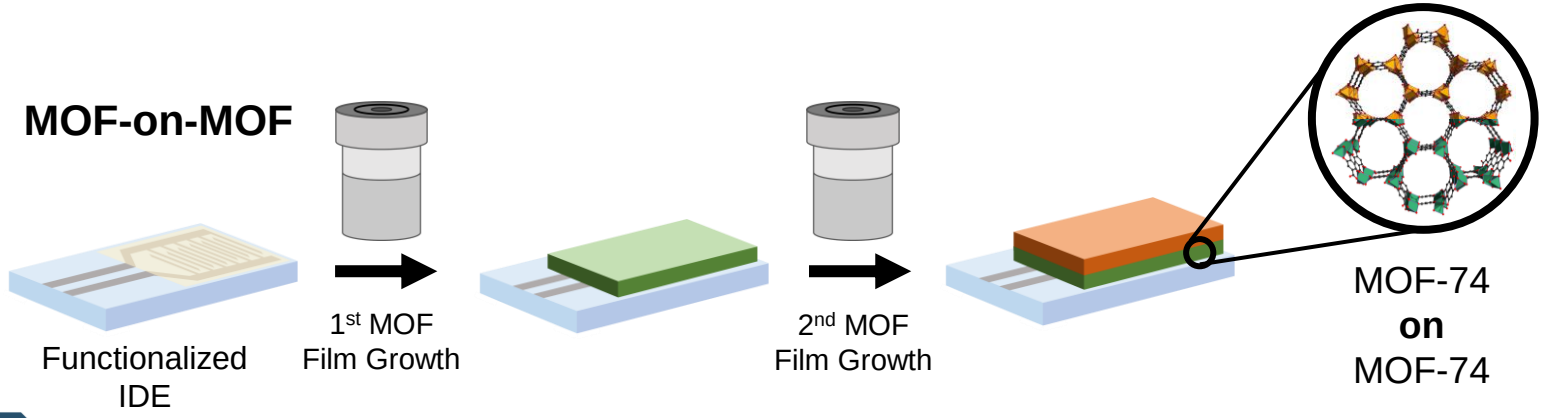
Benefits	Drawbacks
• Any MOF Can Be Used • Less Synthetic Steps • Fast Preparation	• Low Film Control • Low Impedance Response

Thin Film



Benefits	Drawbacks
• High Film Control • Increased Impedance Response • Higher MOF Adherence	• Require Substrate Surface Modification • Additional Synthetic Steps • Challenging for All MOFs

MOF-on-MOF



Benefits	Drawbacks
• Higher MOF Adherence • High Film Control • Improved Film Quality • Highest Impedance Response • Metal Mixing	• Additional Synthetic Steps • Challenging for All MOFs • Require Substrate Surface Modification • Requires Structurally Compatible MOFs

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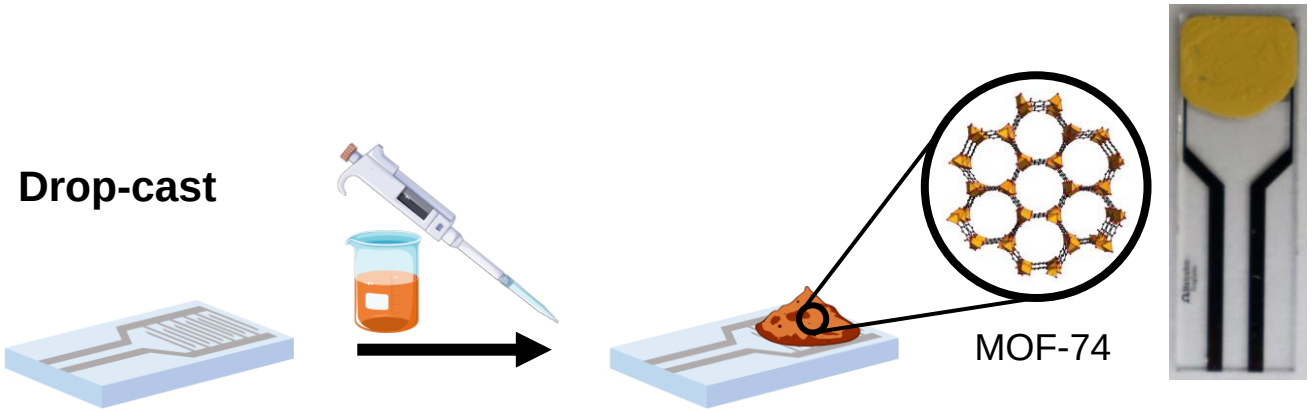
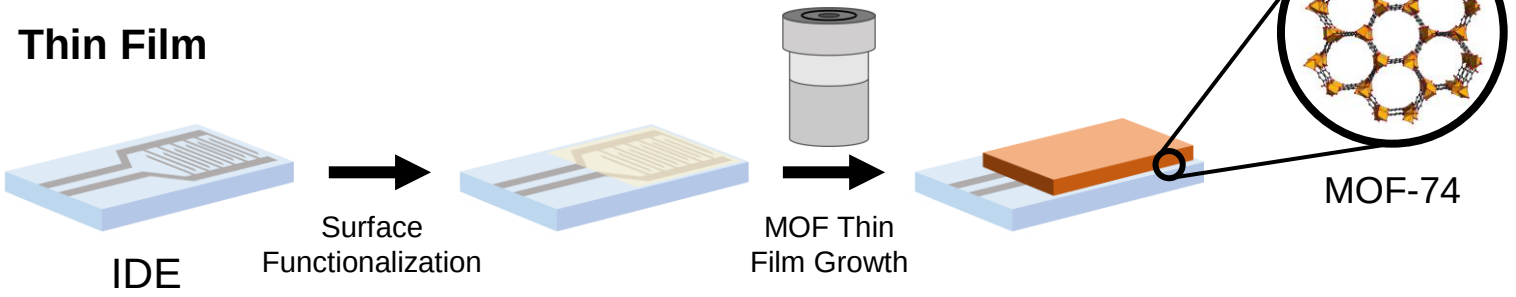
Methods for MOF Thin Film Sensor Synthesis

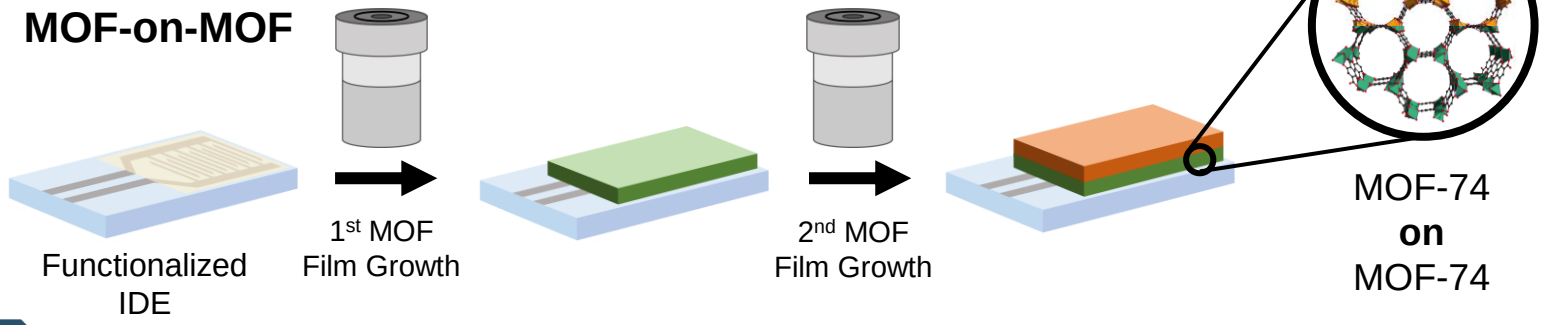
Drop-cast

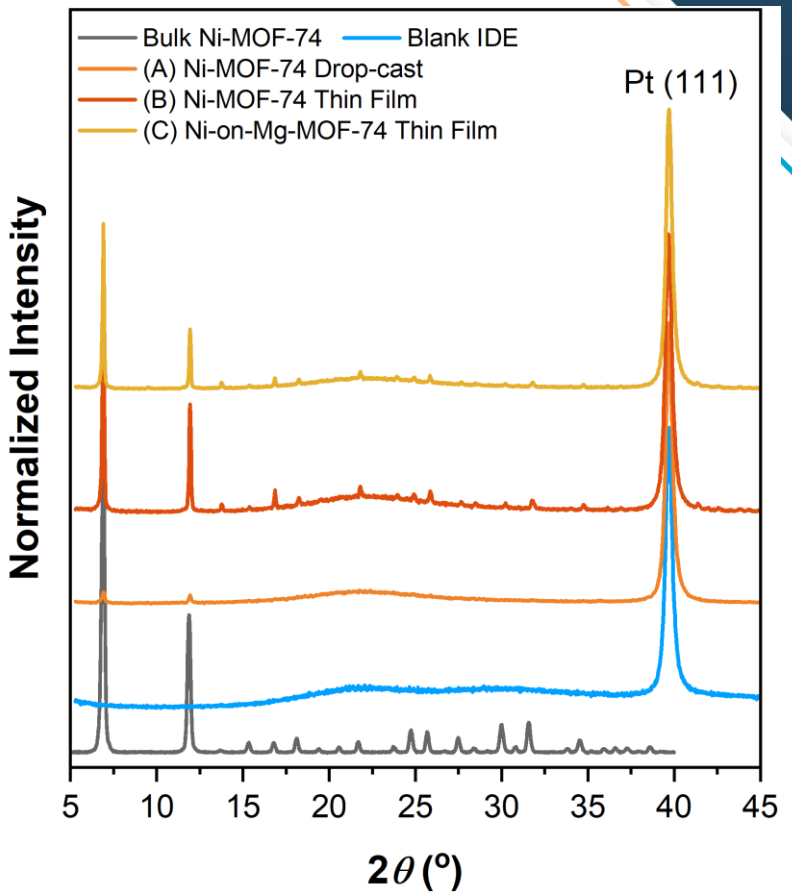


Thin Film



MOF-on-MOF





Mixed metal MOF-74 sensors are achievable with all sensor fabrication methods

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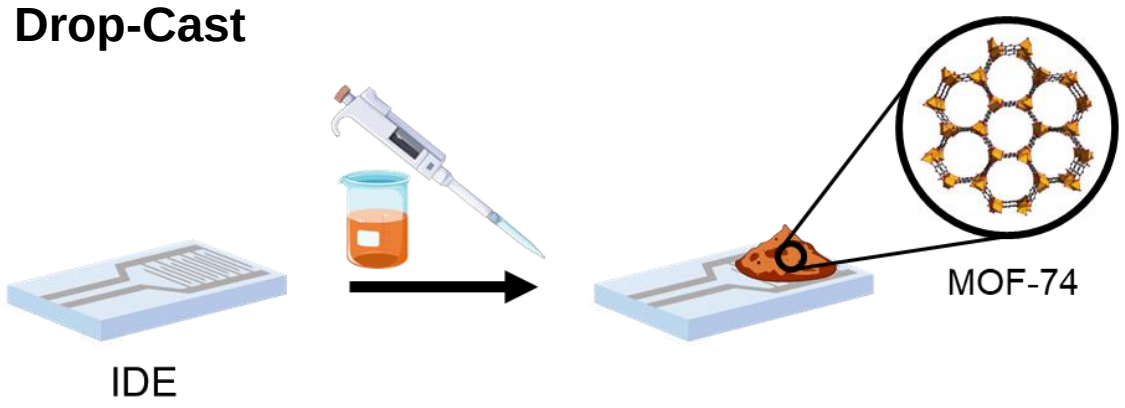
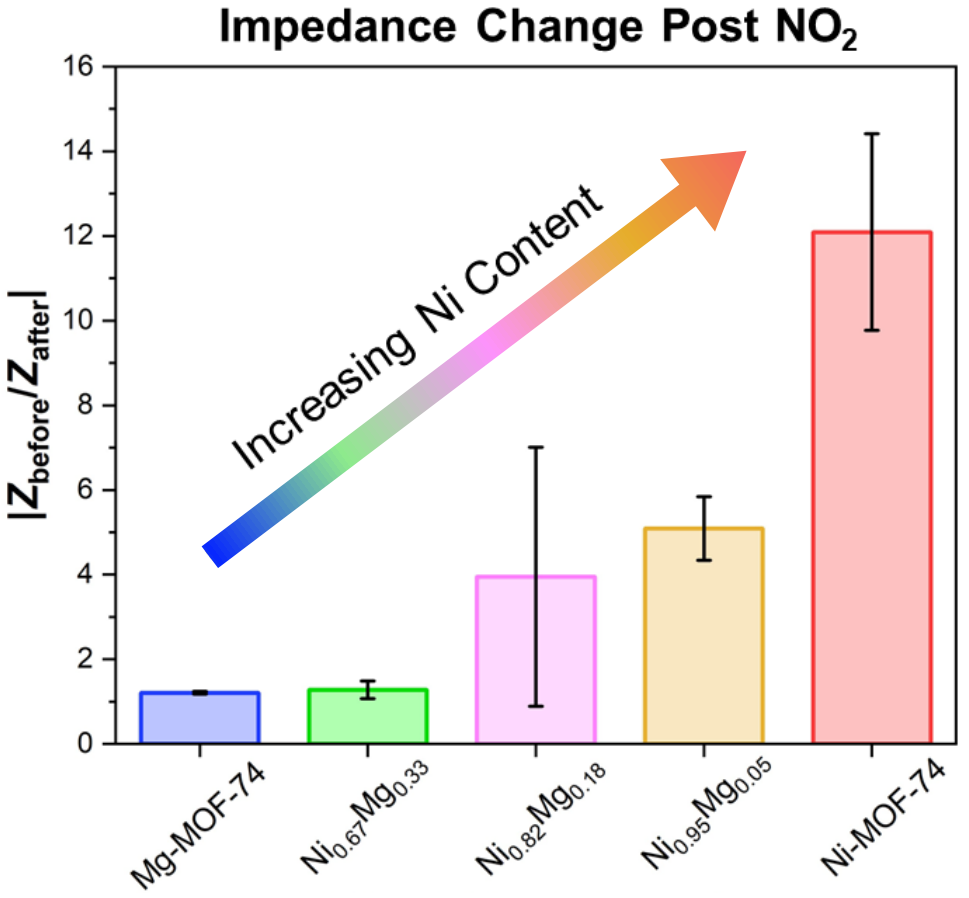
Small Amounts of Mg in Ni-MOF-74 Drop-Cast Sensors Dramatically Impact Performance



- Due to higher stability of Ni-MOF-74 the starting metal ratios needed lower Ni content
- Impedance change upon exposure to 1 ppm NO_2 increased with Ni content
- A 5% Mg content in the MOF-74 framework decreased sensor response over 50%



Mg:Ni ratio within MOF-74 sensors greater than 1:4.5 results in loss of performance

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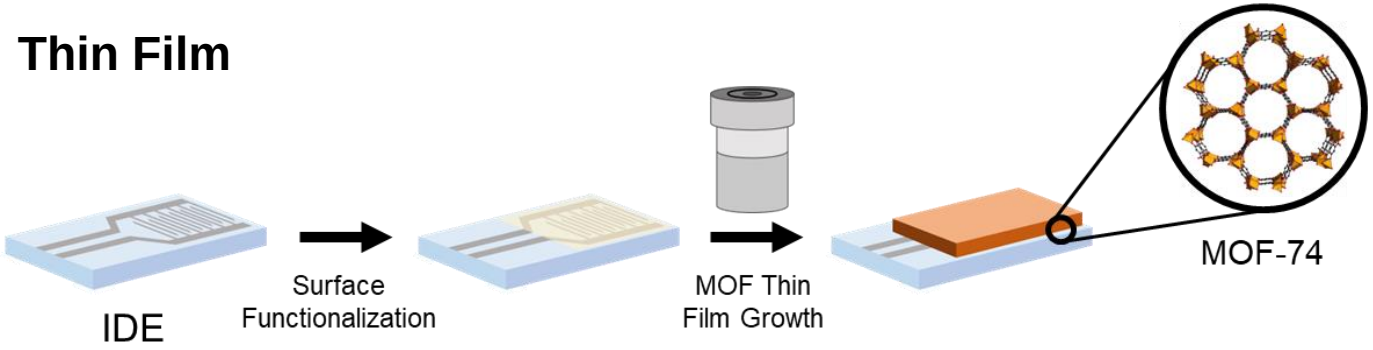
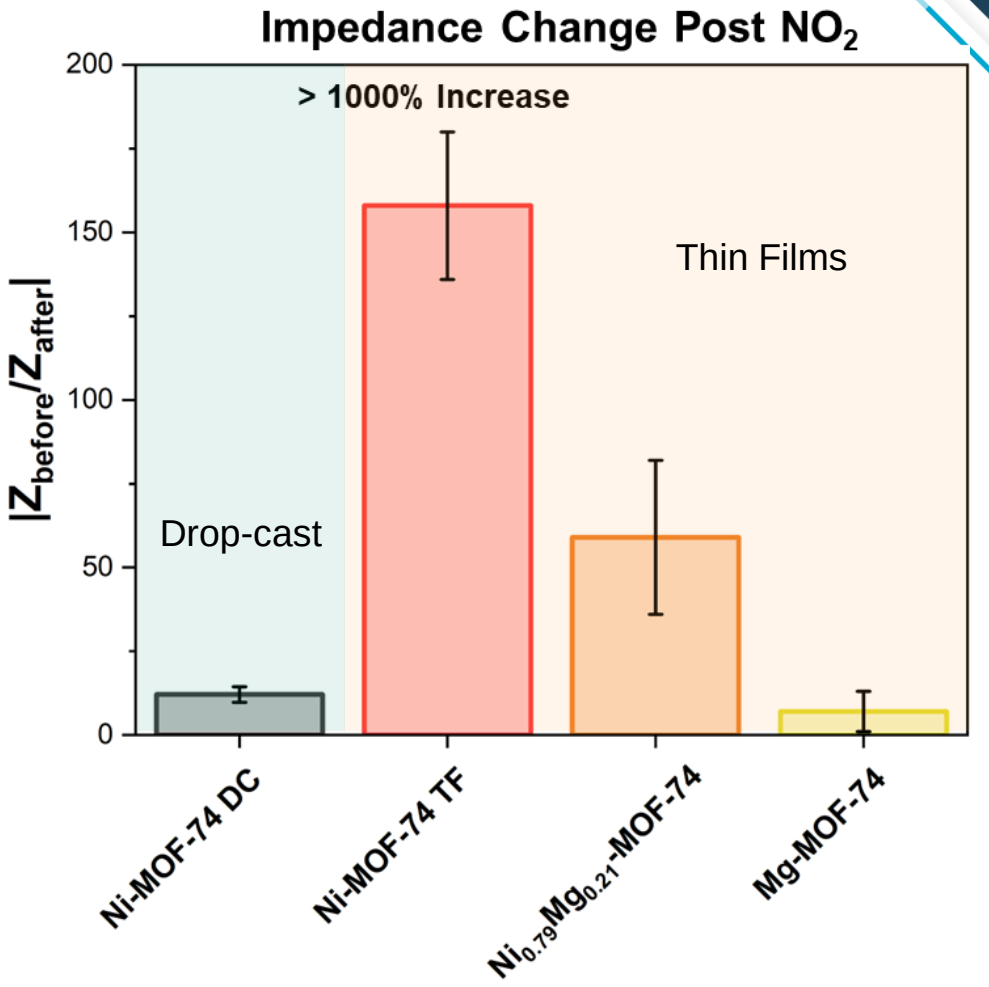
Ni-MOF-74 Thin Film Sensors Showed Three Orders of Magnitude Increase in Impedance Change Toward NO_2





- Thin film sensors showed dramatic performance increase compared to drop-cast
  - Improved 10x from previous thin film sensor generation through synthetic optimization *Membranes,* **2021**, *11*, 3, 176
- Mg-MOF-74 thin film sensors showed lower response compared to Ni-MOF-74 drop-cast sensors
- Thin film sensor performance result of increased MOF-IDE contact and improved film quality

Thin film sensors offer greater response change to NO_2 at larger Mg content in MOF

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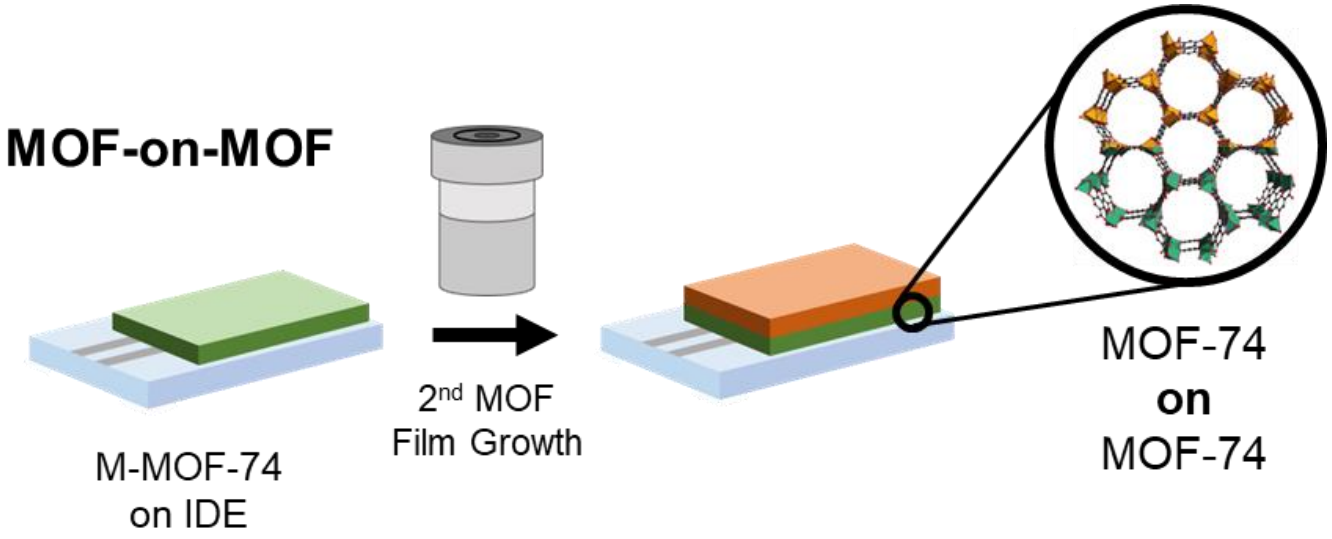
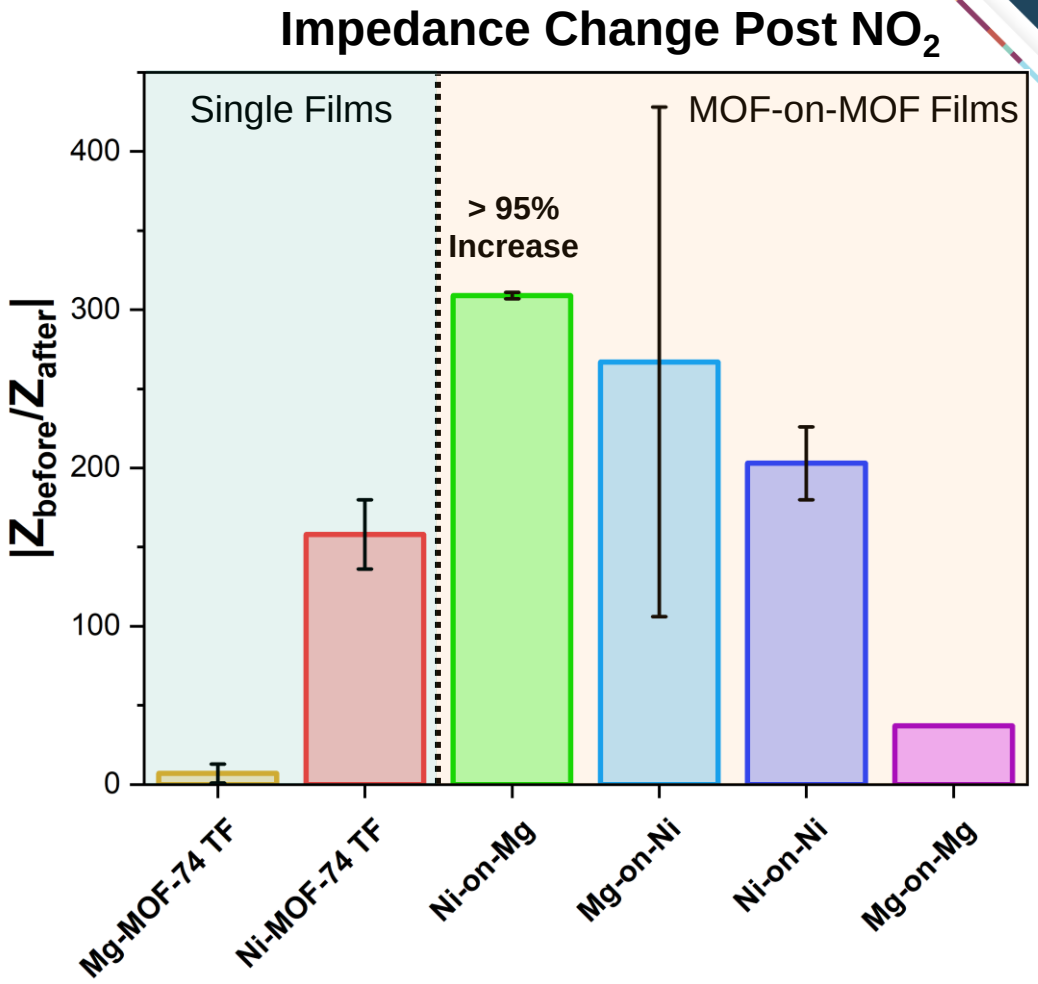
MOF-on-MOF Thin Film Sensors Showed Largest NO_2 Detection Capabilities





- MOF-on-MOF sensors showed dramatic increased impedance change upon trace NO_2 exposure
- Monometallic MOF-on-MOF sensors impedance change increased > 400% and > 25% for Mg and Ni, respectively
- Metal mixing through MOF-on-MOF film synthesis enhanced sensor performance

Hypothesis: MOF-on-MOF synthesis improves film quality, reducing charge scattering sites and increasing impedance change to NO_2 exposure

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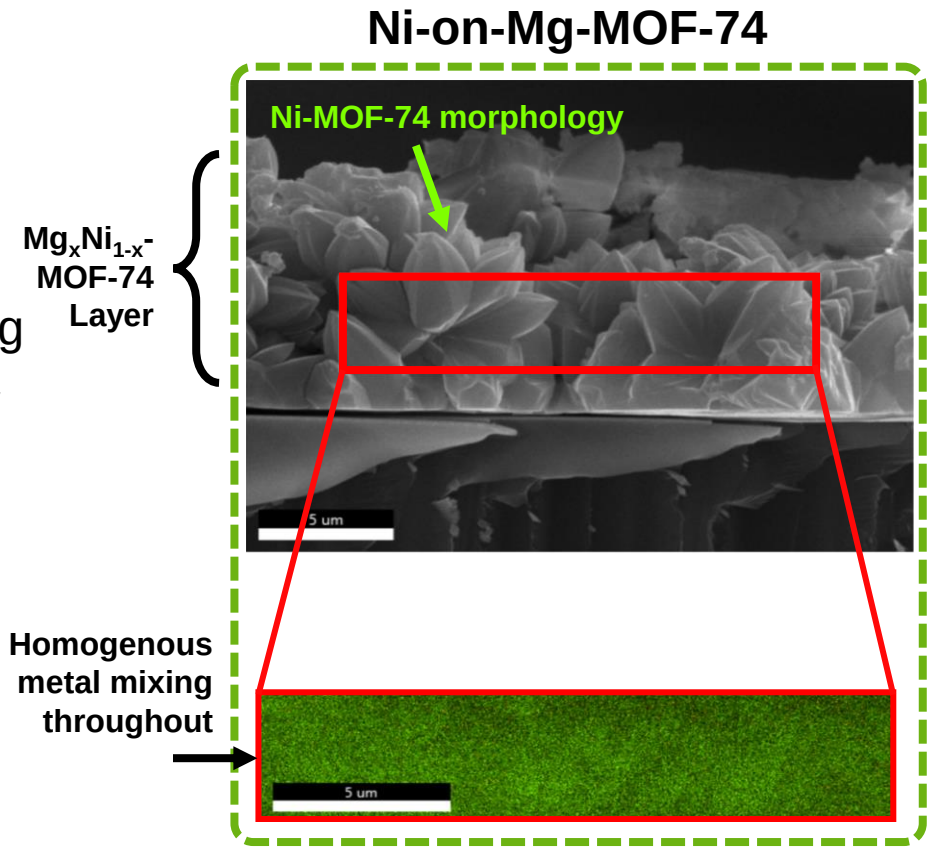
Synthesis Order Influences Metal Mixing Within MOF-on-MOF Thin Films

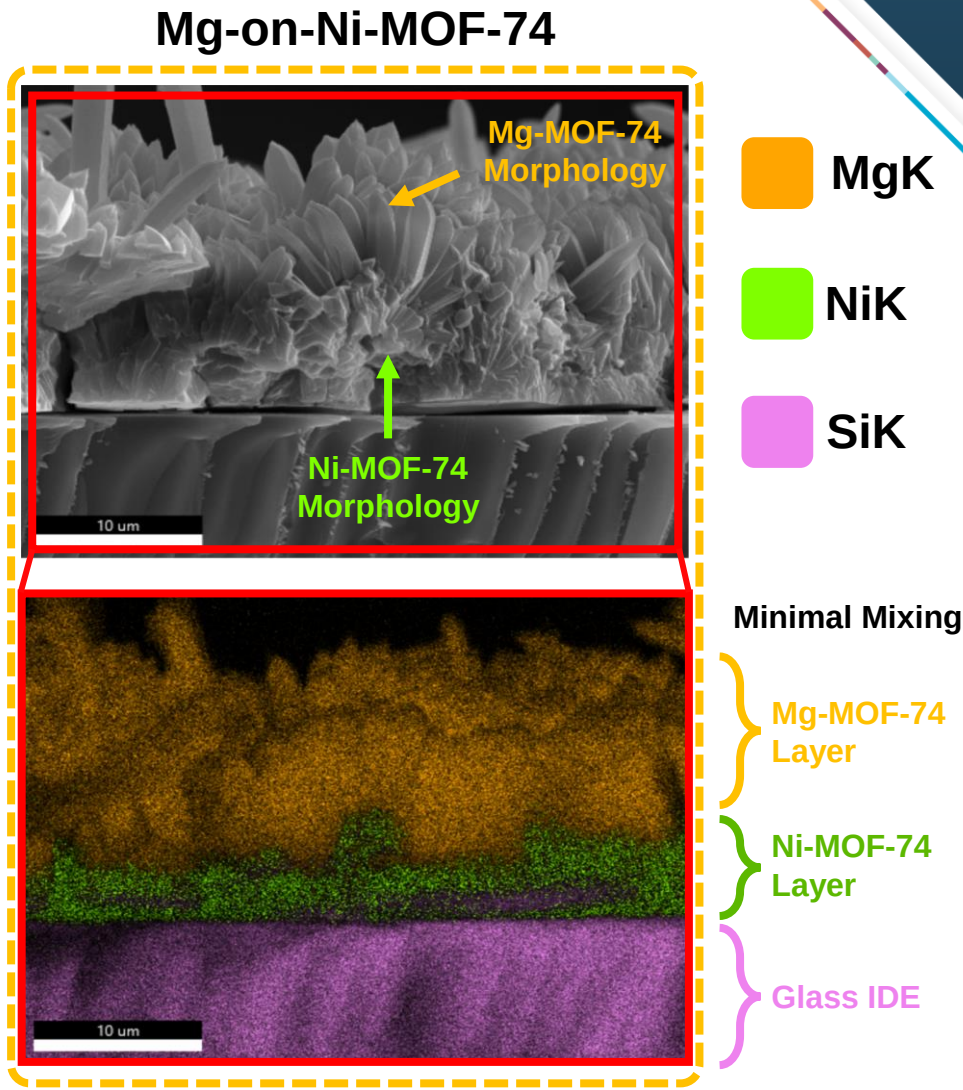
Ni-on-Mg-MOF-74

- Homogenous mixing
- Ni exchanged > 80% Mg
- Ni-MOF-74 morphology dominates

Mg-on-Ni-MOF-74

- Formation of distinct metal layers
- Minimal mixing





Lower stability of Mg-MOF-74 framework led to substantial Ni exchange and thinner film for the Ni-on-Mg sensor

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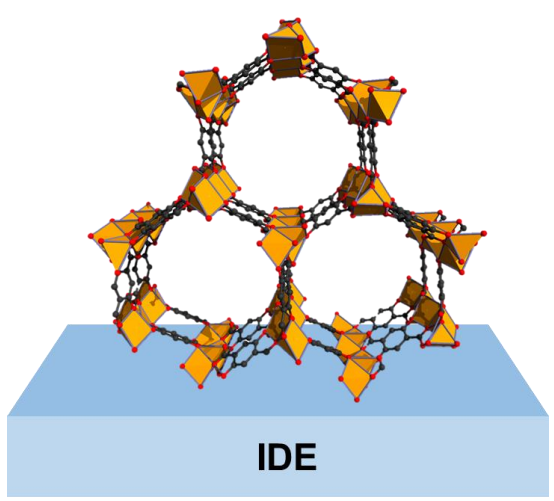
Nanocrystal Orientation of MOF Films Indicates Templating Effect of MOF-on-MOF Synthesis

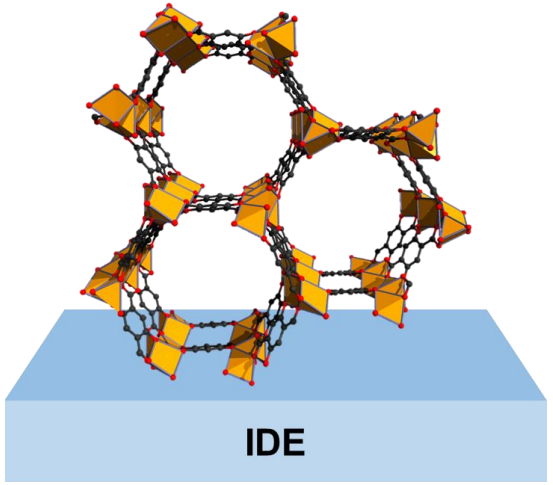
- Orientation preference (OI) of MOF-74 thin films were examined using XRD
  - OI > 1 indicates orientation preference for particular plane
- MOF-on-MOF orientation followed base layer
- Ni-on-Mg films showed no preference

Mg-MOF-74 Preferred the (110) Orientation



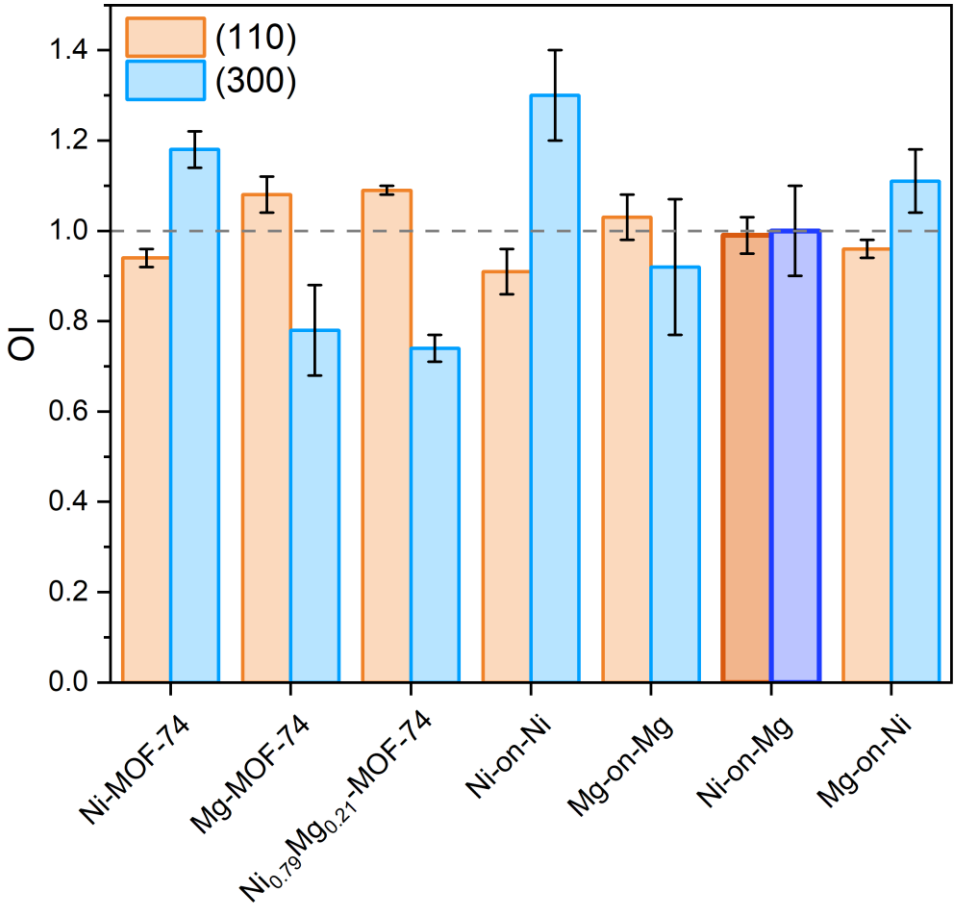
(110) Preferred Orientation

Ni-MOF-74 Preferred the (300) Orientation



(300) Preferred Orientation

Preferred Orientation of MOF-74 Thin Films



Metal exchange during Ni-on-Mg synthesis removes orientation preference

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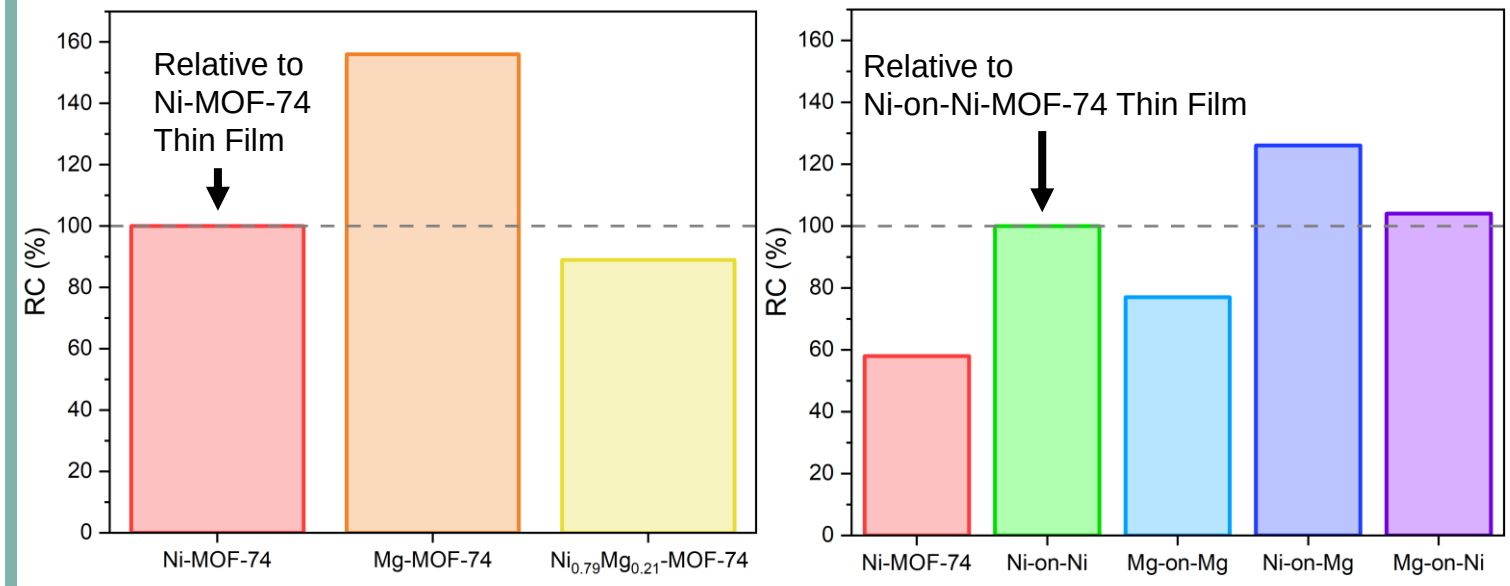
MOF-on-MOF Synthesis Improves Film Quality Leading to Increased Sensor Response

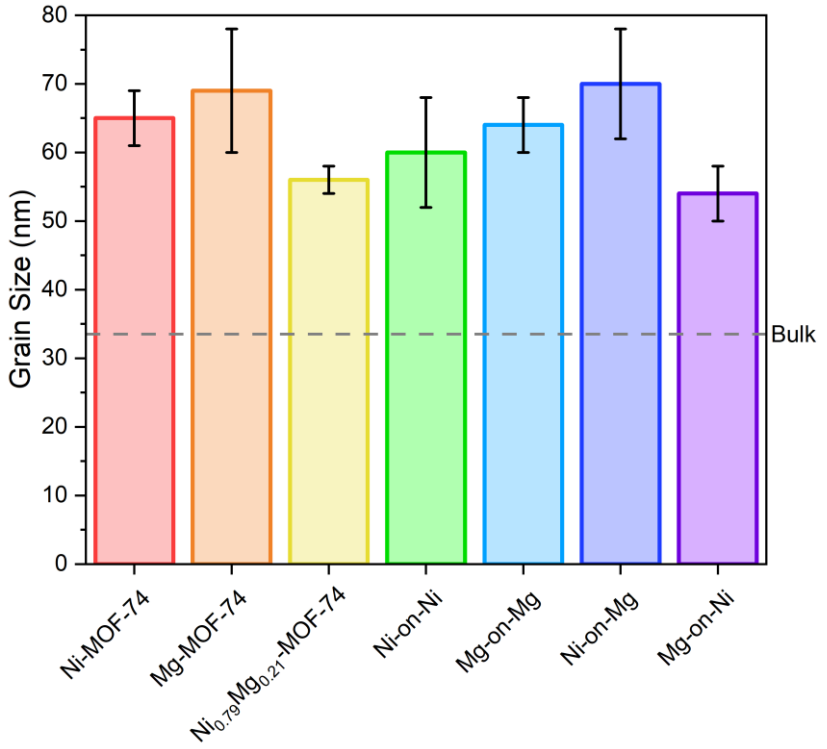
Film quality examined using relative crystallinity and grain size

Relative Crystallinity of Thin Films



- Mg-MOF-74 thin films showed **higher** quality films than Ni
- Direct metal mixing led to decreased film crystallinity
- MOF-on-MOF synthesis increased film crystallinity
- Ni-on-Mg film showed greatest crystallinity

Nanocrystal Grain Size



- Mg-MOF-74 films showed largest grain sizes
- Metal mixing decreased grain size, except Ni-on-Mg
- Large grain size reduces frequency of misaligned grains

Mg-MOF-74 thin film structurally templates the resulting metal exchanged Ni-on-Mg-MOF-74 film

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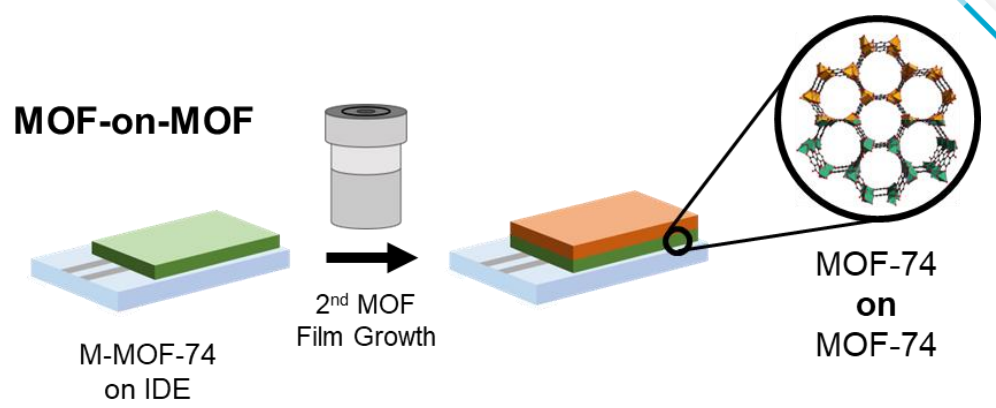
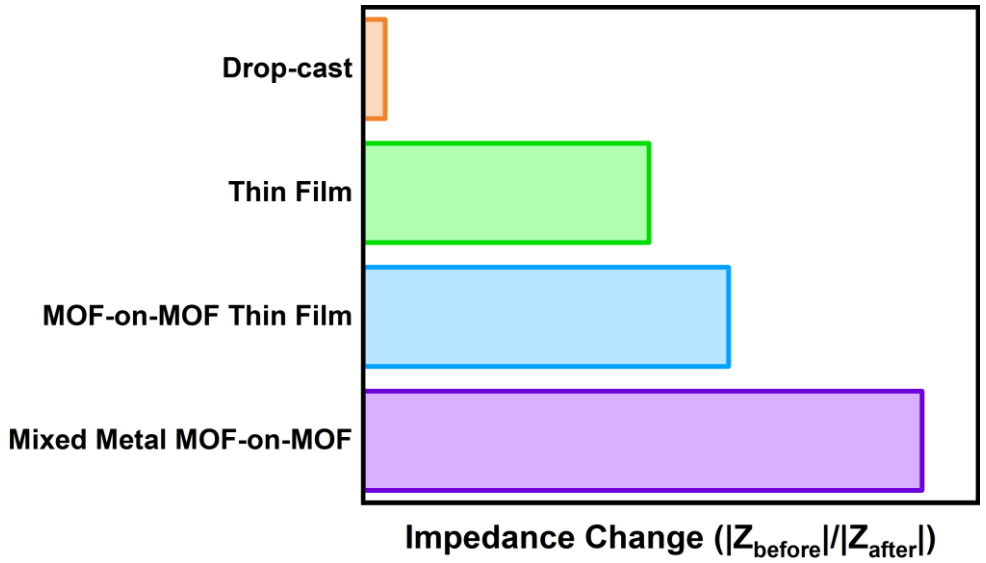
Summary and Outlook

- Demonstrated the capability of M-MOF-74 impedance sensors to detect trace NO_2
- Developed synthetic methods to improve M-MOF-74-based sensors performance for toxic gases
- Elucidated structure-property relationships between film quality and MOF sensor performance



Future and Ongoing Work:

- Identify degradation pathway of M-MOF-74 sensor exposed to trace NO_2
- Iterating new sensor generations using less expensive substrates
- Improving sensing capabilities through development of standalone sensing devices



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