Dimensionally Engineered MOF Films for Chemiresistive Sensors

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Table S1. Comparison of several major types of MOF-based sensors.

Sensor	Mechanism	Advantages	Disadvantages
Chemiresistive	Changes in conductivity	High sensitivity; Low cost; Fast response; Portable; Easy to integrate; Sensor arrays/e-nose; Commercially available; Real-time;	Low conductivity of some MOFs; Susceptible to humidity; Limited sensing range; Poor precision;
Fluorescent/ Phosphorescent	Changes in fluorescence or phosphorescence intensity, lifetime, or emission wavelength	High sensitivity; Multiple response modes; Real-time imaging; Simple instrumentation; Low background signal;	Interfered by environment (pH, temperature) or instrumentation; Potential photobleaching; Poor stability of some MOFs in aqueous media
Quartz Crystal Microbalance (QCM)	Changes in mass	Low work temperature; Portable; Low power consumption; Wide detection range;	Device expensive; Instability; Poor precision; Interfered by humidity and temperature; Poor reproducibility
Surface Plasmon Resonance (SPR)	Binding of analytes to the MOF layer on a metal film alters the refractive index at the interface, causing a shift in the SPR resonance angle or wavelength	Real-time; Label-free detection; High sensitivity; Can monitor binding kinetics	Expensive instrumentation; Sensor chips are often disposable
Electrochemical	MOFs modified on electrode surfaces catalyze the redox reaction of target molecules, leading to changes in current (amperometric), potential (potentiometric), or impedance (impedimetric)	High sensitivity; Low LOD; Low cost; Fast response; Miniaturization	Electrode modification can be complex; Long-term stability affected by electrode fouling; Interference from other electroactive species
IR Spectroscopy	Changes in the IR absorption (frequency/intensity)	High sensitivity; High selectivity; Rich molecular information	Water Interference; Signal Quantification; Equipment cost
Capacitive	Change of capacitance	Low work temperature; Low power; Portable; Cheap;	Low selectivity; sensitive to humidity and temperature; sensor life is limited
FET	Change in current/voltages	Device exibility; Low temperature operation; Compatibility with CMOS; Cost effective; Low power consumption; Real-time	Core MOF materials are yet to be made for high-speed switching; Requires high mobility; subthreshold swing of lower values

Table S2. A comprehensive summary of all organic ligand abbreviations alongside their corresponding full chemical names, as featured in this review.

Ligand Abbreviation	**Full Chemical Name**
HITP	2,3,6,7,10,11-hexaiminotriphenylene
HHTP	2,3,6,7,10,11-hexahydroxytriphenylene
THQ	Tetrahydroxy-1,4-quinone
HIB	Hexaiminobenzene
HIOTP	Hexaamino-triphenyleno[2,3-b:6,7-b’:10,11-b’’]tris[1,4]benzodioxin
HHTT	Hexathioltriphenylene
C_6O_6	Hexaoxotriphenylene
MPc	Metallophthalocyanine
MPy	Metalloporphyrin
TCPP	Tetrakis(4-carboxyphenyl)porphyrin
HAB	Hexaaminobenzene
BHT	Benzenehexathiol
TP	Triphenylene (core structure for HHTP, HITP, etc.)
EDOT	3,4-ethylenedioxythiophene
TCNQ	7,7,8,8-tetracyanoquinododimethane
HHB	Hexahydroxybenzene
DADHA	1,5-diamino-4,8-dihydroxyanthraquinone
H_4DTA	(4,4’-[1,4-phenylenebis-(carbonylimino)]bis(2-hydroxybenzoic acid))
H_4ODA	(4,4’-[oxalylbis(imino)]bis(2-hydroxybenzoic acid)])
BDC	1,4-benzenedicarboxylic acid
HIB	Hexaiminobenzene
NiPc	(2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato) Ni(II)
NiNPc	(3,4,12,13,21,22,30,31-octamethoxynaphthalocyaninato) Ni(II)

Ligand Abbreviation	**Full Chemical Name**
BPDC-SO_2	Dibenzo[b,d]-thiophene-3,7-dicarboxylate 5,5-dioxide
H_2PZDC	1H-pyrazole-3,5-dicarboxylic acid
(γ-CD)	γ-Cyclodextrin
H_3BTB	4,4’,4’’,-benzene-1,3,5-triyl-tris acid
CoPc-OH	(2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato) Cobalt(II)
TBTT-8OH	Octahydroxyl tetraphenylthieno-[3,2-b]thiophene

Table S3. Abbreviations, compositions, and chemical formulas of the MOFs discussed in this review.

MOF	Full name/ Description	Metal Node	Ligand	Chemical Formula
ZIF-67	Zeolitic Imidazolate Framework-67	Co^{2+}	2-methylimidazole	$C_8H_{10}CoN_4$
$Co(Im)_2$	Cobalt-imidazolate framework	Co^{2+}	Imidazolate (Im)	$C_6H_6CoN_4$
Mg-MOFs-I; Mg-MOFs-II	Mg-MOFs	Mg^{2+}	(4,4'-[1,4-phenylenebis-(carbonylimino)]bis(2-hydroxybenzoic acid)) (H_4TDA); (4,4'-[oxalylbis(imino)]bis(2-hydroxybenzoic acid)) (H_4ODA)	$Mg_2(TDA)(H_2O)_2/Mg_2(ODA)(H_2O)_2$
UIO-66	Universitetet i Oslo-66	Zr^{4+}	1,4-benzenedicarboxylic acid (BDC)	$C_{48}H_{28}O_{32}Zr_6$
NH_2-UIO-66	Zr-NH_2-benzenedicarboxylate MOF	Zr^{4+}	2-amino-terephthalic acid	$C_{48}H_{34}N_6O_{32}Zr_6$
OH-UIO-66	Hydroxy-functionalized UIO-66	Zr^{4+}	2-hydroxy-terephthalic acid	$C_{48}H_{28}O_{38}Zr_6$
$Cu_3(HIB)_2$	2D eC-MOF	Cu^{2+}	Hexaiminobenzene (HIB)	$Cu_3(C_{12}H_6N_6)_2$
$M_3(HITP)_2$	2D eC-MOF	Cu^{2+}, Ni^{2+}	2,3,6,7,10,11-hexaiminotriphenylene (HITP)	$M_3(C_{18}H_{12}N_6)_2$
$Cu_3(HHTP)_2$	2D eC-MOF	Cu^{2+}	2,3,6,7,10,11-hexahydroxytriphenylene (HHTP)	$Cu_3(C_{18}H_6O_6)_2$
Cu_3(HHTP)(THQ)	dual-ligand eC-MOF	Cu^{2+}	HHTP and Tetrahydroxy-1,4-quinone (THQ)	$[Cu_3(C_{18}O_6H_6)(C_6O_6)(H_2O)_{11.78}(NH_3CH_2CH_2NH_3)_{1.59}]$
NiPc-M / NiNPc-M	Nickel-phthalocyanine-based eC-MOF	Ni^{2+}	(2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato) Ni(II) (NiPc)/(3,4,12,13,21,22,30,31-octamethoxynaphthalocyaninato) Ni(II) (NiNPc)	$Ni_3C_{32}H_8N_8O_8/Ni_3C_{48}H_{16}N_8O_8$

MOF	Full name/ Description	Metal Node	Ligand	Chemical Formula
PCN-222-M	Metalloporphyrin(MPor)-based MOFs	Zr^{4+}	M-Tetrakis(4-carboxyphenyl)porphyrin (TCPP, a type of MPy) M = Fe, Co, Ni, Cu	-
HIOTP-Ni	eC-MOF with large pores	Ni^{2+}	Hexaamino-triphenyleno[2,3-b:6,7-b':10,11-b'']tris[1,4]benzodioxin (HAOTP)	$Ni_3(C_{36}H_{12}O_6N_6)_2$
Zr-BPDC-SO_2	Sulfone-functionalized Zr-MOF	Zr^{4+}	Dibenzo[b,d]-thiophene-3,7-dicarboxylate 5,5-dioxide (BPDC-SO_2)	-
MIL-53	Matériaux de l'Institut Lavoisier-53	Al^{3+}	1,4-benzenedicarboxylic acid (BDC)	$AlC_8H_5O_5$
$CrCl_2$(pyrazine)$_2$	Cr-MOF	Cr^{2+}	Pyrazine	$CrC_{16}H_{32}N_8Cl_2$
Ni-HAB	Ni-MOF	Ni^{2+}	Hexaaminobenzene (HAB)	-
$Cu_3(C_6O_6)_2$	Paramagnetic MOF	Cu^{2+}	Hexaoxotriphenylene (C_6O_6)	$Cu_3(C_6O_6)_2$
MIL-125	Matériaux de l'Institut Lavoisier-125	Ti^{4+}	Terephthalic acid	$C_{48}H_{24}O_{36}Ti_8$
Cu_3(HHTT)$_2$	Copper-based eC-MOF	Cu^{2+}	2,3,7,8,12,13-Hexahydroxytricycloquinazoline(HHTT)	$Cu_3(C_{18}N_4O_6H_{12})_2$
Ni-CAT-1	Nickel-based 2D eC-MOF	Ni^{2+}	2,3,6,7,10,11-hexahydroxytriphenylene (HHTP)	$Ni_3(C_{18}O_6H_{12})_2$
NH_2-MIL-125(Ti)	Amino-functionalized MIL-125	Ti^{4+}	2-aminoterephthalic acid	$C_{48}H_{34}N_6O_{36}Ti_8$
ZIF-8	Zeolitic Imidazolate Framework-8	Zn^{2+}	2-methylimidazole	$Zn(C_4H_5N_2)_2$
MOF-802	Zr-MOF	Zr^{4+}	1H-pyrazole-3,5-dicarboxylic acid (H_2PZDC)	$C_{39}H_{16}N_{14.5}O_{39}Zr_6$

MOF	Full name/ Description	Metal Node	Ligand	Chemical Formula
Cu-BHT	Copper-benzenehexathiol MOF	Cu^{2+}	Benzenehexathiol (BHT)	$Cu_3C_6S_6$
Bi-gallate MOF	A bismuth-gallate based MOF	Bi^{3+}	Gallic acid	$[Bi(C_6H_4O)_2COOH]_n$
CD-MOF	Cyclodextrin-based MOF	K^+	γ-Cyclodextrin (γ-CD)	-
NUS-8	A 2D zirconium-based MOF	Zr^{4+}	4,4',4'',-benzene-1,3,5-triyl-tris acid (H_3BTB)	$Zr_6O_4(OH)_4(HCOO)_6(BTB)_2$
ZIF-71	Zeolitic Imidazolate Framework-71	Zn^{2+}	4,5-dichloroimidazole	$C_{7.3}H_2Cl_4N_4O_{0.03}Zn$
MIL-101	Materials of Institut Lavoisier-101	Cr^{3+}	1,4-benzenedicarboxylic acid (BDC)	$C_{24}H_{16}Cr_3FO_{15}$
Mpc-O_8-Cu	2D eC-MOF	Cu^{2+}	(2,3,9,10,16,17,23,24-octamethoxyphthalocyaninato) Cobalt(II) (CoPc-OH)	$Cu_2C_{32}H_8O_8N_8Ni$
Cu-MOF-3	2D eC-MOF	Cu^{2+}	Octahydroxyl tetraphenylthieno-[3,2-b]thiophene (TBTT-8OH)	$Cu_2C_{30}O_8H_{12}S_2$
$Mn_2(NiS_4)$	mixed-linker MOF	Mn^{2+}	Ni-bis[1,2-di(4-carboxylphenyl)-1,2-ditholene	$Mn_2(C_{16}H_8O_4S_2Ni)$
Ni-pyz	Hofmann-Type MOF	Ni^{2+}	pyrazine	$Ni_2C_8H_4N_6$
Cu-HHB	2D eC-MOF	Cu^{2+}	Hexahydroxybenzene (HHB)	$C_{12}Cu_3O_{12}$
Cu_2DADHA	1D eC-MOF	Cu^{2+}	1,5-diamino-4,8-dihydroxyanthraquinone (DADHA)	$Cu_2C_{14}H_8N_2O_2$

Table S4. A comparative overview of dimensional engineering strategies for MOF-based chemiresistive sensors, correlating film architecture, fabrication methods, and key sensing performance metrics.

film dimension	**Thick Films**	**2D Thin Films**	**3D Thin Films**
Typical fabrication method	e.g. dip-coating, drop-casting, spin-coating, doctor-blade, vacuum filtration	e.g. Layer-by-layer (LBL) assembly, Liquid-phase epitaxial (LPE) growth, Air-liquid interface, Electrochemical deposition	e.g. solvothermal, growth on 3D substrates
Structure and morphology	Limited exposed area, randomly stacked microcrystals, high surface roughness, macroscopic defects	Oriented channel, nanoscale thickness, low roughness, tight packing, limited exposed area	Oriented channels, expanded exposed area, accessible functional groups
Substrate adhesion	Poor adhesion	Good adhesion	Strong adhesion
Mass/charge transport	Long and torturous path	Short path	Fast charge/mass transport
Operating temperature	Usual medium temperature or room temperature	RT	Can achieve RT operation
Sensitivity	Poor	Moderate	High
LOD	ppm-ppb level	ppb level	ppb-ppt
Response/recovery speed	Slow	Relatively fast	Faster
Core mechanism linkage	Defects and grain boundaries severely limit mass and charge transport; active sites are not fully exposed.	Ordered structure promotes gas diffusion; dense film reduces transport barriers; tunable active interface.	Maximizes the active surface area; provides a vertical and efficient "highway" for mass and charge transport.
Universality	Good universality	Poor universality	Poor universality (complex fabrication, limited current examples)
Cost	Economical	Low efficiency	Complex setups, time-consuming

Table S5. Summary of common types of defects in MOF thick films, their formation mechanisms, and their impact on mass and charge transport.

Defect	Formation mechanism	Mass transport	Charge transport	Sensing performance
Interparticle gaps; voids; microcracks	Random agglomeration; weak interparticle connections; internal stresses generated during solvent evaporation	Creates a non-selective bypass; increasing diffusion tortuosity	Poor signal-to-noise ratio; inefficient charge transport	Low sensitivity; slow response/recovery

Table S6. Comparison of island growth, layer-by-layer growth, and mixed growth modes.

Growth Mode	Island Growth	Layer-by-Layer Growth	Mixed Growth
formation condition	$E_{aa} > E_{as}$	$E_{as} \geq E_{aa}$	initial layer-by-layer + strain relaxation
surface energy relation	$\gamma_{substrate} > \gamma_{film} + \gamma_{film\text{-}substrate}$	$\gamma_{substrate} \geq \gamma_{film} + \gamma_{film\text{-}substrate}$	layer-like initially; energy relation changes later
growth process	3D island nucleation and island coalescence	2D atomic layer-by-layer spreading	initial layer-like and later island transition
film surface morphology	island structures, rough	layered structure, smooth	flat top + island-covered base
film density	low	high	moderate
crystallinity	poor	excellent	fair to good
strain state	low strain	near strain-free	strain-relaxed
typical applications	nanoparticles, rough surfaces	semiconductor epitaxy, optical multilayers	quantum dot self-assembly, heteroepitaxy

Table S7. A comprehensive comparison of prevalent MOF thin film fabrication techniques, with their operational characteristics, advantages, disadvantages, and typical examples.

Method	**Key parameters**	**Advantages**	**Disadvantages**	**Examples**
Seed-assisted solvothermal	Temperature, pressure, reaction time, precursor concentration/ratio, substrate nature, seed layer	Broad applicability, direct synthesis on substrates	Harsh conditions, high energy consumption, not suitable for thermally sensitive substrates; can be time-consuming (hours to days)	NH_2-MIL-125[1]
Chemical vapor deposition	Precursor vapor pressure, substrate temperature, chamber pressure, deposition time	Enables thickness-controlled, uniform film growth; good compatibility with microfabrication	Complex equipment; requires volatile precursors; not all MOFs are suitable	ZIF-8[2]
Exfoliation	Sonication time, solvent choice, layered MOF precursor	Simple procedure, yields ultrathin nanosheets	Low exfoliation efficiency, nanosheet aggregation; may damage crystals	Layered MOFs (e.g., M-TCPP (M = Zn, Cu, Cd or Co)[3]
Electrochemical deposition	Current density, electrolyte composition, reaction time, metal anode type	Mild conditions; easy control of particle size; suitable for continuous production	Requires a conductive substrate; currently limited to a few MOFs (e.g., HKUST-1)	HKUST-1[4]
Layer-by-Layer (LbL) Self-Assembly	Precursor concentration, immersion time, number of cycles, substrate functional groups	Precise control over film thickness and composition; growth on complex 3D substrates	time-consuming; film quality depends on diffusion/coordination kinetics	HKUST-1[5]
Thermal spraying	Spray pressure, nozzle diameter, precursor concentration, substrate temperature, nozzle-to-substrate distance	Convenient, scalable route for large/curved substrates	Film quality is highly dependent on precise control of spraying parameters	2D MOF nanosheets (e.g., Cu-TCPP)[6]
Air/liquid-liquid interfacial synthesis	Reactant concentration, interfacial tension, pH, subphase composition, reaction time	Produces ultrathin, large-area, continuous, defect-free nanofilms; simple operation, low energy cost	Challenges in film transfer	$Cu_3(BTC)_2$[7]

Method	Key parameters	Advantages	Disadvantages	Examples
Microfluidic-based solution shearing	Shear rate, precursor concentration, channel temperature, flow rate	Enables ultra-fast, large-area MOF film growth	Requires specialized microfluidic equipment; process optimization can be complex	$Ni_3(HITP)_2$[8]
Thermal crosslinking	Crosslinking temperature/time, crosslinker type/concentration	Enhances mechanical strength and chemical stability of MOF films	High temperature may damage MOF structure; may reduce porosity	CLIP-MOF[9]
Mixed matrix membrane (MMM)	MOF filler loading, particle size, polymer matrix choice, compatibility	Combines MOF selectivity with polymer processability; tunable performance	Potential interface compatibility issues between MOF and polymer; may form defects	MIL-303)/P84[10]
Liquid-phase epitaxy (LPE)	Precursor concentration, immersion time, substrate functionalization, solvent choice	Produces highly ordered, well-oriented films; precise thickness control	time-consuming; requires specific substrate functionalization	$Cu_3(HHTP)_2$[11]
Bottom-up modular assembly	Module ratio/combination (metal node, ligand, template), reaction conditions (pH, temperature)	Highly tunable structure, easy multifunctionality; enables large-scale synthesis, ultrathin	Complex; requires precise control of reaction conditions	bis(dipyrrinato)zinc(II)[12]

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