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Review article

Lanthanide Metal-Organic Frameworks for Humidity Sensing Applications

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Keywords

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Abstract

Metal-organic frameworks (MOFs) for humidity sensing have continued to receive intense interest over the past several years. MOFs have attracted worldwide attention in the area of sensing, particularly for humidity sensing. MOFs are a family of nanoporous materials and class of compounds. MOFs have higher surface area and porosity, low densities, flexible and tuneable porous structure, these are the attractive properties for gas sensing. For these reasons MOFs have been extensively studied. The review focuses on experimental studies. In this review, an overview on sensing performance of relative humidity sensors based on synthesized MOFs are presented.

Introduction

Humidity sensor is an electronic device that measures the humidity in its environment and converts its findings into a corresponding electrical signal. It varies widely in size and functionality; some humidity sensors can be found in handheld devices (such as smartphones), while others are integrated into larger embedded systems (such as air quality monitoring systems).

Humidity sensors can be divided into two groups, as each category uses a different method for calculating humidity: relative humidity (RH) sensors and absolute humidity (AH) sensors. A humidity sensor is a device that senses, measures and reports the relative humidity (RH) of air or determines the amount of water vapor present in a gas mixture (air) or pure gas (Ekta poonia et al. 2019).

MOFs for humidity sensing

Humidity sensors have many significant applications in daily life, such as medicine, biology, meteorology, agriculture, and many others. Humidity sensors with accurate humidity control play a vital role in different industrial processes, food packaging, environmental monitoring, automotive control systems and equipment maintenance because of variations in moisture requirements.

Many research works have been represented involving humidity sensors towards advancing performance in recent years. Humidity sensing materials comprising semiconductors, perovskite oxides, and polymers have presently attracted the scientific community's attention. Among these materials, perovskite oxides humidity sensors based have shown high reliability and sensitivity (P. Jena et al. 2011, M.P. Suh et al. 2011, M. Murialdo et al. 2019).

Many commercial humidity sensors are available to perceive volatile constituents at ppm-level concentrations but still, humidity sensing below ∼100 ppm (few percentages relative humidity (RH) at 298 K) encounter challenges. In many applications such as medicinal provisions, gas and fuel storage, agricultural products storage, semiconductor manufacturing, humidity sensing is obligatory at ppm or ppb level (J. Zhang et al. 2017, T.I. Nasution et al. 2018, M. Zhang et al. 2017, M.S. Hosseini et al. 2019).

In the case of MOFs-based humidity sensors, only few reports exist to the best of our knowledge. Therefore, there is a need to explore and optimize suitable MOFs that are highly desirable and can operate in various environments under different conditions. Following MOF materials have been studied as humidity sensors: CAU-10 with different functional groups on the linker (Weiss A et al. 2015), HKUST-1 showed a low detection limit of 5.45 ppm or MIL-96(Al) which was applied as a smart textile-based sensor (TEX sensor) on different types of textiles (Rauf S et al. 2020).

In general, compounds MOF-76(Ln) (Ln = lanthanide) with a chemical formula $\{[Ln(BTC)(H_2O)]\cdot G\}$ (BTC = benzene-1,3,5-tricarboxylate/trimesate, G = guest molecule) represent a family of homeotypic porous lanthanide metal-organic frameworks. Compounds were studied as gas adsorbents for carbon dioxide (M. Almáši et al. 2015, P.F. Santos et al. 2020, C. Zhang et al. 2019, J. Ethiraj et al. 2016) methane (P.F. Santos et al. 2020, A.S. Chevinly et al. 2017), hydrogen (A. Garg et al. 2021) and ammonia. As heterogeneous catalysts in knoevenagel condensation, cyanosylilation (M. Gustafsson et al. 2010), esterification, isomerisation (T. Kiyonaga et al. 2015), oxidative desulfurization reactions and synthesis of ammonia (C. Zhang et al. 2019). Due to the specific luminescent and fluorescent properties of lanthanide ions in the MOF-76(Ln) framework, these materials find an interesting application as sensors (X. Lian et al. 2016, Y. Yang et al. 2020, D. Wu et al. 2019, B. Chen et al. 2007). Searching the databases, several studies focused on sensing of cations (Nd(III), Cu(II) and U(VI), anions (F(-I), Cl(-I), Br(-I), NO_3(-I), CO_3(-II) and SO_4(-II)), drugs (nitroimidazole, quinolone and nitrofuran antibiotics, dipicolinic acid, cefixime), aromatic pollutants (J. Yang et al. 2006, M. Almáši et al. 2017, V. Zeleňák et al. 2019, L.H. Xie et al. 2011, S. Liu et al. 2020, T. Kajiwara et al. 2014) such asmonoaromatic hydrocarbons, small organic molecules (dimethylformamide, acetone and ethanol), methanol and pesticides (chlorpyrifos) were published [R.R.F. Fonseca et al. 2019, H. Eskandari et al. 2018, J. Li et al. 2018, T. Lee et al. 2013, W. Yang et al. 2013, W. T. Yang et al. 2012, H. Eskandari et al. 2020). Other fields of applications where MOF-76(Ln) compounds were tested are magnetism, electrochemical hydrogen and oxygen production and photocatalytic degradation of ammonia [N.L. Rosi et al. 2005, Chen L et al. 2008, X. Guo et al. 2006, Q. Zhou et al. 2013, M. Almáši et al. 2016, Kajiwara T et al. 2014).

Sr. No.	**Materials**	**Type**	**RH range**	**Response Time (s)**	**Recovery Time (s)**
1.	$Bi_{3.25}La_{0.75}Ti_3O_{12}$	Oxide	11–95%	8	250
2.	$K_{0.5}Na_{0.5}NbO_3$	Oxide	11-95%	8	18
3.	Co-TiO_2	Oxide	11–95%	32	131
4.	$Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}Ti_{0.97}Zr_{0.03}O_3$	Oxide	11–95%	18	60
5.	$SnWO_4$-SnO_2	Oxide	11–98%	30	100
6.	LiCl/SBA-15	Silica	11–95%	21	51
7.	MCM-48	Silica	11–95%	29	107
8.	NaCl/KIT-6	Silica	11–95%	47	150
9.	QCM/HKUST-1	MOF	22–69%	1676	1051

10.	MWCTN/HKUST-1	MOF	5–75%	250	265
11.	HKUST-1	MOF	11–84%	20	20
12.	EuM	MOF	53–100%	390	400
13.	MIL-101(Cr)	MOF	33–95%	17	90
14.	MIL-101(Cr)-NH_2	MOF	11-95%	15	130
15.	MIL-125(Ti)-NH_2	MOF	11–95%	45	50
16.	**MOF-76(Gd)**	**MOF**	**11–98%**	**11**	**2**

Conclusion

Currently MOFs have been considered as a new member of nanoporous materials that recently have attracted all the consideration to materials chemistry. It is clear that MOFs will present exceptional advantages compared to other conventional porous materials and it will have a significant impact on the future of porous compounds. Typically under mild reaction conditions, these techniques can be use for some materials, which leads to the production of compounds with different features and particles sizes. The challenges and orientations present the continual expansion interest and a bright future of MOF chemistry.

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References

1. Garg, M. Almáši, D.R. Paul, E. Poonia, J.R. Luthra, A. Sharma. Metal-organic framework MOF-76(Nd): Synthesis, characterization and study of hydrogen storage and humidity sensing. Front. Energy Res., 8 (2021) 604735.
2. A.S. Chevinly, H.G. Mobtaker, T. Yousefi, A.S. Shirani, H. Aghayan. {[Ce(BTC)(H2O)]·DMF}n metal organic framework as a new adsorbent for removal of neodymium ions. Inorg. Chim. Acta, 455 (2017) 34.
3. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian, E. B. Lobkovsky. Luminescent open metal sites within a metal–organic framework for sensing small molecules. Adv. Mater., 19 (2007) 1693.
4. Zhang, Y. Xu, C. Lv, X. Zhou, Y. Wang, W. Xing, Q. Meng, Y. Kong, G. Chen. Mimicking π backdonation in Ce-MOFs for solar-driven ammonia synthesis. ACS Appl. Mater. Interf., 11 (2019) 29917.

5. Chen, L. Wang, F. Zapata, G. Qian, E. B. Lobkovsky. A luminescent microporous metal−organic framework for the recognition and sensing of anions. J. Am. Chem. Soc., 130 (2008) 6718.
6. Wu, Z. Zhang, X. Chen, L. Meng, C. Li, G. Li, X. Chen, Z. Shi, S. Feng. A nonluminescent Eu-MOF-based “turn-on” sensor towards an anthrax biomarker through single-crystal to single-crystal phase transition. Chem. Commun., 55 (2019) 14918.
7. Ekta Poonia, Vijay Kiran, Jasbir Sangwan, Surender Duhan, and Krishan Kumar. Enhanced Sensing Performance of Relative Humidity Sensors Based on Mn/KIT-6 Hybrid Nanocomposite. Sensor Letters 17, 1–6, 2019. http://doi:10.1166/sl.2019.4071.
8. H. Eskandari, M. Amirzehni, H. Asadollahzadeh, J. Hassanzadeh, P.A. Eslami. MIP capped terbium MOF-76 for the selective fluorometric detection of cefixime after its preconcentration with magnetic graphene oxide. Sens. Actuat. B: Chem., 275 (2018).
9. H. Eskandari, M. Amirzehni, J. Hassanzadeh, B. Vahid. Mesoporous MIP-capped luminescent MOF as specific and sensitive analytical probe: application for chlorpyrifos. Microchim. Acta, 187 (2020) 673.
10. J. Ethiraj, F. Bonino, J.G. Vitillo, K.A. Lomachenko, C. Lamberti, H. Reinsch, K.P. Lillerud, S. Bordiga. Solvent-driven gate opening in MOF-76-Ce: Effect on CO2 adsorption. Chem Sus Chem, 9 (2016) 713.
11. J. Li, X. Yuan, Y. Wu, X. Ma, F. Li, B. Zhang, Y. Wang, Z. Lei, Z. Zhang. From powder to cloth: Facile fabrication of dense MOF-76(Tb) coating onto natural silk fiber for feasible detection of copper ions. Chem. Eng. J., 350 (2018) 637.
12. J. Yang, Q. Yue, G. D. Li, J.J. Cao, G. H. Li, J. S. Chen. Structures, photoluminescence, up-conversion, and magnetism of 2D and 3D rare-earth coordination polymers with multicarboxylate linkages. Inorg. Chem., 45 (2006) 2857.
13. J. Zhang, L. Sun, C. Chen, M. Liu, W. Dong, W. Guo, S. Ruan. High performance humidity sensor based on metal organic framework MIL-101(Cr) nanoparticles. J. Alloys Comp., 695 (2017) 520.
14. Kajiwara T, Higuchi M, Watanabe D, Higashimura H, Yamada T, Kitagawa H (2014) A systematic study on the stability of porous coordination polymers against ammonia. Chem Eur J 20:15611-15617. https://doi.org/ 10.1002/chem.201403542.
15. L.H. Xie, Y. Wang, X.M. Liu, J.B. Lin, J.P. Zhang, X.M. Chen. Crystallographic studies into the role of exposed rare earth metal ion for guest sorption. Cryst Eng Comm., 13 (2011) 5849-5857.

16. M. Almáši, V. Zeleňák, A. Zeleňáková. Magnetic and structural studies into the effect of solvent exchange process in metal-organic framework MOF-76(Gd). Acta Phys. Pol.A, 131 (2017) 991.
17. M. Almáši, V. Zeleňák, J. Kuchár, S. Bourrelly, P. Llewellyn. New members of MOF-76 family containing Ho(III) and Tm(III) ions: Characterization, stability and gas adsorption properties. Colloids Surf. A: Physicochem. Eng. Aspects, 496 (2016) 114.
18. M. Almáši, V. Zeleňák, M. Opanasenko, I. Císařová. Ce(III) and Lu(III) metal-organic frameworks with Lewis acid metal sites: Preparation, sorption properties and catalyticactivity in Knoevenagel condensation. Cat. Today, 243 (2015) 184.
19. M. Gustafsson, A. Bartoszewicz, B. Martín-Matute, J. Sun, J. Grins, T. Zhao, Z. Li, G. Zhu, X. Zou. Family of highly stable lanthanide metal−organic frameworks: Structural evolution and catalytic activity. Chem. Mater., 22 (2010) 3316.
20. M. Murialdo, N.J. Weadock, Y. Liu, C.C. Ahn, S.E. Baker, K. Landskron, B. Fultz. High-pressure hydrogen adsorption on a porous electron-rich covalent organonitridic framework. ACS Omega., 4 (2019) 444.
21. M. Zhang, S. Wei, W. Ren, R. Wu. Development of high sensitivity humidity sensor based on gray TiO2/SrTiO3 composite. Sensors, 17 (2017) 1310
22. M.P. Suh, H.J. Park, T.K. Prasad, D.W. Lim. Hydrogen storage in metal-organic frameworks. Chem. Rev., 112 (2011) 782.
23. M.S. Hosseini, S. Zeinali. Capacitive humidity sensing using a metal–organic framework nanoporous thin film fabricated through electrochemical in situ growth. J. Mater. Sci.: Mater. Electronics, 30 (2019) 3701.
24. N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O.M. Yaghi. Rod packings and metal−organic frameworks constructed from rod-shaped secondary building units. J. Am. Chem. Soc., 127 (2005) 1504.
25. P. Jena. Materials for hydrogen storage: Past, present, and future. J. Phys. Chem. Lett.,2 (2011) 206.
26. P.F. Santos, J. Ribeiro, P.P. Luz. Physicochemical and electrochemical characterization of Ce/carbonaceous matrices-based composites. Solid State Sci., 110 (2020) 106479.
27. P.F. Santos, P.P. Luz. Synthesis of a Ce-based MOF-76 with high yield: A study of reaction parameters based on a factorial design. J. Braz. Chem. Soc., 31 (2020) 566.
28. Q. Zhou, F. Yang, B. Xin, G. Zeng, X. Zhou, K. Liu, D. Ma, G. Li, Z. Shi, S. Fenga. Reversible switching of slow

magnetic relaxation in a classic lanthanide metal–organic framework system. Chem. Commun., 49 (2013) 8244.

29. R.R.F. Fonseca, R.D.L. Gaspar, I.M. Raimundo Jr., P.P. Luz. Photoluminescent Tb3+ based metal-organic framework as a sensor for detection of methanol in ethanol fuel. J. Rare Earths, 37 (2019) 225.
30. Rauf S, Vijjapu MT, Andrés MA, Gascón I, Roubeau O, Eddaoudi M, Salama KN (2020) Highly selective metal–organic framework textile humidity sensor. ACS Appl Mater Interf 12:29999-30006. https://doi.org/ 10.1021/acsami.0c0753.
31. S. Liu, X. Lia, H. Zhang. Synergistic effects of MOF-76 on layered double hydroxides with superior activity for extractive catalytic oxidative desulfurization. New J. Chem.,(2020) 6269.
32. T. Kajiwara, M. Higuchi, D. Watanabe, H. Higashimura, T. Yamada, H. Kitagawa. A systematic study on the stability of porous coordination polymers against ammonia. Chem. Eur. J., 20 (2014) 15611.
33. T. Kiyonaga, M. Higuchi, T. Kajiwara, Y. Takashima, J. Duan, K. Nagashimac, S. Kitagawa. Dependence of crystal size on the catalytic performance of a porous coordination polymer. Chem. Commun., 51 (2015) 2728.
34. T. Lee, H. L. Lee, M. H. Tsai, S. L. Cheng, S. W. Lee, J. C. Hu, L. T. Chen. A biomimetictongue by photoluminescent metal–organic frameworks. Biosens. Bioelectr., 43 (2013).
35. T.I. Nasution, I. Nainggolan, D. Dalimunthe, M. Balyan, R. Cuana, S. Khanifah. Humidity detection using chitosan film-based sensor. IOP Conf. Series: Mat. Sci. Eng., 309 (2018) 012080.
36. V. Zeleňák, M. Almáši, A. Zeleňáková, P. Hrubovčák, R. Tarasenko, S. Bourelly, P. Llewellyn. Large and tunable magnetocaloric effect in gadolinium-organic framework: tuning by solvent exchange. Sci. Rep., 9 (2019) 15572.
37. W. T. Yang, J. Feng, S. Y. Song, H. J. Zhang. Microwave-assisted modular fabrication of nanoscale luminescent metal-organic framework for molecular sensing. Chem Phys Chem, 13 (2012) 2737.
38. W. Yang, Z. Q. Bai, W. Q. Shi, L. Y. Yuan, T. Tian, Z. F. Chai, H. Wang, Z. M. Sun. MOF-76: from a luminescent probe to highly efficient UVI sorption material. Chem. Commun., 49 (2013) 10415.
39. Weiss A, Reimer N, Stock N, Tiemann M, Wagne T (2015) Surface-modified CAU-10 MOF materials as humidity sensors: impedance spectroscopic study on water uptake. Physic Chem Chem Phys

17:21634–21642. https://doi.org/10.1039/c5cp01988e.

40. X. Guo, G. Zhu, Z. Li, F. Sun, Z. Yang, S. Qiu. A lanthanide metal–organic framework with high thermal stability and available Lewis-acid metal sites. Chem. Commun., 30(2006) 3172.
41. X. Lian, B. Yan. A lanthanide metal–organic framework (MOF-76) for adsorbing dyes and fluorescence detecting aromatic pollutants. RSC Adv., 6 (2016) 11570.
42. Y. Yang, L. Zhao, M. Sun, P. Wei, G. Li, Y. Li. Highly sensitive luminescent detection toward polytypic antibiotics by a water-stable and white-light-emitting MOF-76 derivative. Dyes Pig., 180 (2020) 108444.