Metal-Organic Framework as a New Photocatalyst for Environmental Pollutant Treatment

Chenghao Ying
Ningbo Xiaoshi High School, China
*Corresponding author e-mail: samuel1265629622@outlook.com

Abstract. Metal-organic frameworks (MOFs) which are novel and burgeoning porous crystalline materials. In recent researches, MOFs demonstrated a variety of applications due to their unique features: large surface area and tunable porosity. The unique features have attracted extensive researching interests in exploring the application of MOFs as photocatalysts for environmental remediation. Herein, the review starts with an overview of fundamental aspects of MOFs followed by the introduction of several synthesizing techniques. The discussion of MOFs characteristics and their applications in photocatalysis will be focused on.

Key words: Metal-organic Framework; Photocatalysis.

1. Introduction
With the current world economic development, especially given current population growth and the expanding industries to cause pollution, manifest economic growth is at the expense of environmental pollution. In order to achieve long-term sustainable development, environmental pollution is a challenge which is urgent needed to resolved. There are various sources of environmental pollution, but strategies for remediation are lacking. Therefore, the development of a new, cost-effective, and environmentally friendly strategy has become crucial. The pollution materials generally include all types of organic compounds, such as organic dyes, pesticides, hydrocarbons, fertilizers, detergents, plasticizers, oils, medicines, etc. At present, treatment methods focus on adsorption, microbial treatment, membrane filtration, flocculation, and so on. Advanced Oxidation Process (AOP), which is one of the most promising measures to remove tenacious compounds present in wastewater treatment effluents [1], meanly relies on the breakdown of chemical bond with free radicals. Conventional advanced oxidation techniques, such as the Fenton reaction, produce large amounts of iron sludge and require a narrow opening of pH. Therefore, we need to develop a green and applicable technology to solve the environmental problems.

Photocatalysis is a green technology with non-secondary pollution and efficient degradation of pollutants. Photocatalysis involves the irradiation of light of appropriate wavelength onto semiconductor materials. The release of electrons to Conduction Bands (CB) and Valence Bands (VB) excites charge carriers to perform redox reactions to produce electron-hole pairs to react with water, oxygen molecules or hydroxyl groups to create reactive oxygen species or hydroxyl free radicals to destroy pollutants into small, non-toxic, biodegradable molecules. The photocatalysis is contributed by the photoexcitation, which is possible when the photocatalyst gets the enough amount of energy to reach equal to its band
gap energy level, and the transfer of electrons from the VB to CB own in Figure 1. [2, 3]. In order to achieve the photocatalysis, there are basically four steps contributed to the breakdown of the pollutants: (1) Formation of e-\textendash h+ as a result of photoexcitation; (2) e- recombination in absence of no electron acceptor; (3) Photo-induced electron transportation and reduction of oxygen; (4) Oxidation due to hole in VB, while 3.2 eV is Eg between VB and CB. [4]

![Figure 1](image_url)  
**Figure 1.** Primary mechanism of photocatalysis of pristine semiconductor sphere illustrating different steps [4]  

In general, the size of energy gap is the key factor of photocatalyst materials. Various photocatalyst materials have been explored, such as metal oxide (TiO$_2$), quantum dots (CdS, carbon quantum dots), and carbon nitride (C$_3$N$_4$). Metal Organic Frameworks (MOFs) have become one of the most promising materials in the field of photocatalytic applications in recent studies. MOFs are a kind of porous material mixed with inorganic and organic ligands and metal ions or clusters to form two-dimensional or three-dimensional structures through chemical bonds. Permanent porous structures and channels provide anchored active centers for photocatalytic reactions and give them the structural characteristics and functions required for photocatalysis. Due to the chemical properties of its adjustable pore size and the physical characteristics of its large surface area, therefore, MOFs can become a potential material for photocatalytic reactions.

1.1. Hydro/Solvothermal Method

As a conventional synthesis of MOFs, hydro/solvothermal method has been proven to be effective and efficient in the last decades. Considered as a distinctive wet-chemical synthesis method, hydro/solvothermal synthesis needs to be executed in a sealed environment (e.g. autoclave) with water or organic solvent as a medium. In addition, in order to regulate the yield and promote the crystallinity of the as-synthesized materials, the internal temperature needs to be controlled within the range of 100-240 °C. [5] Moreover, based on the hydro/solvothermal theory, non-solid-state reactions is the unique part of the synthetic reactions. The evaporation of reagents at high temperature and the formation of the varying vapor pressure contribute to the feature. Therefore, we are able to prepare novel materials with special valence states, metastable structure, condensed and aggregation states or to make morphology manageable. [6] The attributes of the reagents, including polarity, viscosity and dielectric constants, have substantial effects on the reactions. The interactions of the solvents with the reagents, intermediates, and products would strongly influence the equilibriums and kinetics. Frequently, the mixtures of water, DMF, polyols, oleylamine, methanol are used for the solvents as a result of their out-standing compatibility. [7]

1.2. Microwave-assisted Synthesis

Microwave is an electronic wave which is universally used as a media to transfer energy. Microwave-assisted synthesis method can reduce the time and increase the yield. [8] Microwave radiation is able to heat up reagents hastily, reducing reaction time and increasing the conversion rate. Hence, the spike in
temperature allows fast nucleation rates. However, the formation of agglomerated particles from high microwave temperatures can diminish the available surface area and decrease MOFs adsorption performance. [9] Under microwave irradiation, owing to the thermal effect, the reaction time of UiO-67 under microwave irradiation was much shorter than that of conventional solvothermal methods which would take 24 h for example. In addition, by comparing to resulting materials of conventional heating methods in aspects of porous properties, morphology, gas adsorption capacities, it is proved the successful synthesis of UiO MOFs by microwave heating methods. It is shown that the micro-wave assisted method is an effective alternative to synthesize highly crystalline UiO MOFs by utilizing two indicators of STY and RME to assess the efficiency of the developed microwave synthesis. [10] Zhang et al. synthesized cobalt-based zeolitic imidazolate framework (ZIF-67) taking the advantages of coupling solvent-free and microwave treatments. During the synthesis, the use of organic solvent has been removed and the time taken has been diminished to less than 30 min, showing the great potential in improvement. [11]

1.3. Ultrasound-assisted Synthesis
Ultrasound (US) is defined as cyclical mechanical vibration with a frequency between 20 kHz and 10 MHz. The development of formation, growth, and eventual collapse of bubbles is called cavitation, leading to the rapid release of energy with heating and cooling effects. [12] By utilizing cavitation, it facilitates effective collisions and simplifies the reaction mechanism with the help of product crystallization. The process also makes coordination reaction possible, contributing to a more rapid and more homogeneous crystal growth. [13] In recent researches, it was reported that the ultrasound-assisted synthesis of composites of MOFs, specifically HKUST-1, with activated carbon or molecularly imprinted polymers which acquires strong absorbance capacity. [14, 15] Additionally, TMU-55 and HTMU-55 are typical two zinc(II)-based Fluorinated metal organic frameworks (F-MOFs). They can be prepared via ultrasound-assisted synthesis. The synthesis of TMU-55 and HTMU-55 were performed in an ultrasonic bath under a room temperature and atmosphere pressure with a power output of 305 W. A solution of zinc(II) acetate dihydrate with the various concentration in DMF (10ml) was placed in the ultrasonic bath in order to prepare the different T-MOFs. Then, a mixed-ligand solution of 4,4'- (hexafluoroisopropylidene) and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene or 1,4bis(4-pyridyl)-2,3-diaza-1,3-butadiene in DMF dropwise were added into the solution and sonicated for 60 min, shown in Figure 2. [16]

![Figure 2. The synthetic route used for the synthesis of TMU-55 and HTMU-55 [16]](image_url)

1.4. Electrochemical Method
Electrochemical with its unique characteristics has gained attention. For the industrial advantages, electrochemical synthesis facilitates metal salt-free and continuous production. [17]. Early in 1999, Chui et al. have examined the formation of HKUST-1 thin films on Cu electrode based on anodic dissolution method. The electrosynthesis was conducted in a two-electrode configuration. When an anodic voltage is applied, the elemental copper is oxidized to copper ions and released into the solution containing 1,3,5-benzenetricarboxylate to form HKUST-1. [18] Denayer et al. have electrochemically synthesized HKUST-1 layers on copper mesh without applying any metal salts. [19] A formation of HKUST-1 on
the surface of the electrode via electrochemical synthesis with the form of films is proved feasible. [20, 21]

1.5. Mechanochemical Synthesis
Mechanochemistry, which is reaction sustained or induced by the introductions of mechanical energy, is a promising synthetical method that promote the rate of reactions between solids both rapidly and quantitatively. [22] Mechanochemical synthesis offers inimitable means to prepare a diversity of crystalline materials from coordination networks to hydrogen boned adducts etc., including synthesizing MOFs efficiently in a shortened reaction time requiring little or no solvent. [23, 24] The nonappearance of bulk solvent indicates that mechanochemical reactions are able to readily occur regardless of the relative solubilities of starting materials and products, enabling room temperature synthesis of MOFs. [25] Unlike conventional synthesis of MOFs which was based on solution, mechanochemical synthesis is advantageous for its eco-friendly, clean, and energy-efficient features. [24, 26-29]

2. MOFs Application in Photocatalysis
Photocatalysis, as a unique type of heterogeneous catalysis driven by solar energy, transforms solar energy to chemical energy which can be used for initiation of various types of reactions. Therefore, a variety of applications can be expected from photocatalysis, such as carbon dioxide (CO₂) reduction, water reduction/oxidation, and organic pollutant degradation. [30-34]

2.1. Gas Production and Reduction
With the current severe global warming resulted from excessive emission of CO₂, it is crucial to find a measure to alleviate the intense situation. Wang et al. has synthesized the MOFs catalyst for photochemical CO₂ reduction by direct combination of a catalytic component, [Re(I)(CO)₃(dcbpy)Cl] (dcbpy = 2, 2'-bipyridine-5, 5'-dicarboxylic acid), with UiO-67. [35] And in 2017, Choi et al. synthesized zirconium0-based UiO-67 which was stemmed with two different functional units (Re(I)(CO)₃(BPYDC)Cl, BPYDC=2,2'-bipyridine-5,5'-dicarboxylate) together as a holistic construct. By coating the synthesized material with Ag nanoparticles, the CO₂ reduction ability was promoted from the aspects of stability and catalytic activity. [36] Yan et al. integrated Eu-Ru(phen)₃-MOF (phen=phenanthroline) with the triangular Ru(phen)₃-derived tricarboxylate ligand as photosensitizer into Eu-MOF with Eu(μ₂-H₂O) secondary building units. [37]

Hydrogen is the alternative fuel substantially stored in sea water which is more abundant and environmental-friendly with the possibility of having a lower cost than the fossil fuel. [38] The hydrogen evolution from water reduction with the presence of a photocatalyst is a potential method to facilitate the displacement of fossil fuels. Bhakta et al. has designed a MOFs photocatalyst Ru₂(1,4-BDC)₂ (1,4-BDC=1,4 benzenedicarboxylic acid) for inducing hydrogen evolution from water under the exposure of visible light. [39] Pattengale et al. have reported a spectroscopic study based on the atomic-scale mechanism of ZIF-67 with outstanding activity in the hydrogen evolution reaction (HER). [40] Alfonso Herrera et al. demonstrated the possibility of hydrogen evolution under solar light by utilizing BDC-Zn MOFs. Shown in Figure 3, the combination of methyl orange (MO) /methylene blue (MB) molecules linkers with BDC-Zn MOFs can capture the light from the solar stimulator. The transference of electrons from the conduction to the valence band is introduced by the irradiation of light. The process produced a hole formed in the CB which oxidizes water molecules, and the electron in the VB reduce H⁺ to H₂, releasing hydrogen gas into the surrounding. [41]
2.2. Water-pollution Treatment

Photoactive MOFs are gaining increasing attention for the photocatalytic decomposition of organic pollutants due to their modifiable structural construction and considerable surface area and porosity. Among them, Fe-contained MOFs have been studied widely due to the abundant containment of iron in earth and the iron-oxo clusters present in Fe-based MOFs show an extensive range in visible region. Multiple researches have shown Fe$_3$-$\mu_3$-oxo clusters which are normally contained in MOFs are predominant in the field of photocatalysis, especially the degradation of organic pollutant presented in water bodies, with their small band gap and the presence of Fe(II) in the structure. Laurier et al. has proven Iron(III)-based MOFs’ exceeding photocatalytic performance via the degradation of Rhodamine 6G in aqueous solution. The Fe(III)-MOFs are capable to absorb photons with energy equal or higher than their HOMO-LUMO (Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital) gap which is equivalent to the band gap of conventional semiconductor-based photocatalysis.

Shown in Figure 4, MOFs based on iron(III) oxide have a significant high visible light photocatalytic activity. Among them, MIL-88B(Fe) which indicated the most considerable photocatalytic degradation capacity toward organic dye, Ph6G, is composed with Fe$_3$-$\mu_3$-oxo clusters interconnected by oxidation-stable terephthalate linkers which are responsible for the photocatalytic performance. However, MIL-100(Fe) as a member of MOFs demonstrated relatively low photocatalytic activity at green and red wavelength, but comparable results at other wavelengths. Sun et al. synthesized another MIL-53(Fe) material. In order to examine the catalytic performance, three MOFs samples are selected: NH$_2$-MIL-53(Fe), MIL-53(Fe) and Fe(BDC)(DMF). By utilizing the degradation of the phenol with hydrogen peroxide as an oxidant, the converted phenol is more than 90%. The conversions of hydrogen peroxide
and chemical oxygen demand for Fe(BDC)(DMF) were significantly high among the three MOFs. [44] Wang et al. had modified MIL-125(Ti) by adopting 2-aminoterephthalic acid as organic linker and graphitic carbon nitride as the supporter for growth. [45, 46] It demonstrated an outstanding photocatalytic activity for Cr(VI) reduction and dye mineralization in wastewater under the irradiation of light. Based on the modification, the group synthesized core-shell In$_2$S$_3$@MIL-125(Ti) (MLS) and examined its photocatalytic activity. Under the visible light illumination, In$_2$S$_3$ can be readily excited due to its narrow band gap energy, generating electrons (e$^-$) and holes (h$^+$). The reduction of Ti$^{4+}$ to Ti$^{3+}$ can be introduced through the transfer of photo-generated electrons to Ti$^{4+}$ in the titanium-oxo cluster of MIL-125(Ti) via the heterojunction structure. With oxygen molecules are absorbed into porous MIL-125(Ti), superoxide ($\cdot$O$_2$) are produced via electron transfer from Ti$^{3+}$ to O$_2$ due to the potent reducing ability of Ti$^{2+}$. Antibiotics, like tetracycline (TC), are extensively applied in human health, animal husbandry and fish farming against infectious diseases. However, they indirectly introduce the appearance of antibiotic-resistant pathogens and lead to serious problems for human health and ecosystem balance within the aqueous system. [47] Therefore, photodegradation of TC is an urgent problem to be solved due to its potential threats to the human community. In order to examine the photocatalytic activity of MLS under visible light illumination and find a feasible solution to the TC treatment, a photodegrading experiment of TC have been carried out. [48]

3. Conclusion

This review summarized the functionality of MOFs in the field of photocatalysis used for environmental treatment. In addition, methods to synthesize MOFs are briefly introduced in the previous paragraphs. Although the application of MOF-based materials in the environmental treatment is in its early and undeveloped stage, the materials still hold a great promising future to tackle with the environmental problems. Herein, two main applications of MOF-based materials in photocatalytic environmental treatment have been discussed. MOF-based materials with their outstanding performance in industrial clean-energy production and organic-pollutant disposal have attracted significant researching attention, demonstrating a novel measure for environment remedy. However, due to the restricted reaction conditions, some of the materials would not be produced in a large scale, which could be impractical for massive deployment. Nevertheless, in the foreseeable future, with massive efforts in the modification and improvement of production of MOFs, MOF-based photocatalysts will become one of the potent materials to enhance the environment.

References

[1] P. Bajpai, in Pulp and Paper Industry (2017), pp. 187-192.
[2] J. Krýsa, M. Baudys, X. Vislocka and M. Neumann-Spallart, Catalysis Today 340, 34-39 (2020).
[3] M. R. D. Khaki, M. S. Shafeeyan, A. A. A. Raman and W. M. A. W. Daud, Journal of Environmental Management 198, 78-94 (2017).
[4] J. R. a. M. X. Fatima Imtiaz, in Concepts of Semiconductor Photocatalysis, edited by A. K. Mohammed Rahman, Abdullah Asiri and Inamuddin Inamuddin (Intechopen, 2019).
[5] K. Parvez, in Biomedical Applications of Graphene and 2D Nanomaterials (2019), pp. 1-25.
[6] S. H. Feng and G. H. Li, in Modern Inorganic Synthetic Chemistry (2017), pp. 73-104.
[7] W. Ouyang, A. R. P. Santiago, K. Cerdán-Gómez and R. Luque, in Photoactive Inorganic Nanoparticles (2019), pp. 109-138.
[8] P. P. Bag, X. S. Wang and R. Cao, Dalton Trans 44 (26), 11954-11962 (2015).
[9] G. H. Albuquerque and G. S. Herman, Crystal Growth & Design 17 (1), 156-162 (2016).
[10] R. Vakili, S. Xu, N. Al-Janabi, P. Gorgojo, S. M. Holmes and X. Fan, Microporous and Mesoporous Materials 260, 45-53 (2018).
[11] H. Zhang, J. Zhong, G. Zhou, J. Wu, Z. Yang and X. Shi, Journal of Nanomaterials 2016, 1-9 (2016).
[12] N. Stock and S. Biswas, Chem Rev 112 (2), 933-969 (2012).
[13] R. Klee, M. Wiatrowski, M. J. Aragon, P. Lavela, G. F. Ortiz, R. Alcantara and J. L. Tirado, ACS
Appl Mater Interfaces 9 (2), 1471-1478 (2017).

[14] A. Asfaram, M. Ghaedi and K. Dashtian, Ultrason Sonochem 34, 640-650 (2017).
[15] F. N. Azad, M. Ghaedi, K. Dashtian, S. Hajati and V. Pezeshkpour, Ultrason Sonochem 31, 383-393 (2016).
[16] M. Joharian and A. Morsali, Journal of Solid State Chemistry 270, 135-146 (2019).
[17] A. Martinez Joaristti, J. Juan-Alcañiz, P. Serra-Crespo, F. Kapteijn and J. Gascon, Crystal Growth & Design 12 (7), 3489-3498 (2012).
[18] S. M.-F. L. S.S.-Y. Chui, J.P. Charmant, A.G. Orpen, I.D. Williams, Science 283, 1148-1150 (1999).
[19] T. R. C. Van Assche, G. Desmet, R. Ameloot, D. E. De Vos, H. Terryn and J. F. M. Denayer, Microporous and Mesoporous Materials 158, 209-213 (2012).
[20] H.-m. Yang, X. Liu, X.-l. Song, T.-l. Yang, Z.-h. Liang and C.-m. Fan, Transactions of Nonferrous Metals Society of China 25 (12), 3987-3994 (2015).
[21] C. Allen, S. V. Sambasivarao and O. Acevedo, J Am Chem Soc 135 (3), 1065-1072 (2013).
[22] S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Frisic, F. Grepioni, K. D. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell, Chem Soc Rev 41 (1), 413-447 (2012).
[23] D. Lv, Y. Chen, Y. Li, R. Shi, H. Wu, X. Sun, J. Xiao, H. Xi, Q. Xia and Z. Li, Journal of Chemical & Engineering Data 62 (7), 2030-2036 (2017).
[24] D. Braga, S. L. Giaffreda, F. Grepioni, A. Pettersen, L. Maini, M. Curzi and M. Polito, Dalton Trans (10), 1249-1263 (2006).
[25] T. Friščić, in Encyclopedia of Inorganic and Bioinorganic Chemistry (2014), pp. 1-19.
[26] G. Kaupp, in Organic Solid State Reactions (2005), pp. 95-183.
[27] D. Prochowicz, K. Sokolowski, I. Justyniak, A. Kornowicz, D. Fairen-Jimenez, T. Friščić and J. Lewiński, Chemical Communications 51 (19), 4032-4035 (2015).
[28] D. Prochowicz, I. Justyniak, A. Kornowicz, T. Kaczorowski, Z. Kaszkur and J. Lewinski, Chemistry 18 (24), 7367-7371 (2012).
[29] M. Klimakow, P. Klobes, A. F. Thünenemann, K. Rademann and F. Emmerling, Chemistry of Materials 22 (18), 5216-5221 (2010).
[30] Y. Jia, C. Sun, Y. Peng, W. Fang, X. Yan, D. Yang, J. Zou, S. S. Mao and X. Yao, Journal of Materials Chemistry A 3 (16), 8294-8299 (2015).
[31] R. Asahi, T. Morikawa, H. Irie and T. Ohwaki, Chem Rev 114 (19), 9824-9852 (2014).
[32] C. Chen, W. Ma and J. Zhao, Chem Soc Rev 39 (11), 4206-4219 (2010).
[33] Y. Wang, X. Wang and M. Antonietti, Angew Chem Int Ed Engl 51 (1), 68-89 (2012).
[34] M. D. Hernández-Alonso, F. Fresno, S. Suárez and J. M. Coronado, Energy & Environmental Science 2 (12) (2009).
[35] C. Wang, Z. Xie, K. E. deKrafft and W. Lin, J Am Chem Soc 133 (34), 13445-13454 (2011).
[36] K. M. Choi, D. Kim, B. Rungtaweeveranit, C. A. Trickett, J. T. Barmanbek, A. S. Alshammarri, P. Yang and O. M. Yaghi, J Am Chem Soc 139 (1), 356-362 (2017).
[37] X. Li, X. Yang, H. Xue, H. Pang and Q. Xu, EnergyChem 2 (2) (2020).
[38] A. G. Stern, International Journal of Hydrogen Energy 43 (9), 4244-4255 (2018).
[39] R. K. Bhakta, Herberg, J. L., Jacobs, B., Highley, A., Behrens, R., and N. W. Ockwig, Greathouse, J. A., Allendorf, M. D., J. Am. Chem. Soc. 131, 13198-13199 (2009).
[40] B. Pattengale, S. Yang, S. Lee and J. Huang, ACS Catalysis 7 (12), 8446-8453 (2017).
[41] P. K. C. R. Luis Angel Alfonso Herrera, Ali M. Huerta Flores , Leticia Torres Martinez, Jose Maria Rivera Villanueva,, Materials Science in Semiconductor Processing 109, 1049-1050 (2020).
[42] L. Zeng, X. Guo, C. He and C. Duan, ACS Catalysis 6 (11), 7935-7947 (2016).
[43] K. G. Laurier, F. Vermoortele, R. Ameloot, D. E. De Vos, J. Hofkens and M. B. Roefflaers, J Am Chem Soc 135 (39), 14488-14491 (2013).
[44] Q. Sun, M. Liu, K. Li, Y. Zuo, Y. Han, J. Wang, C. Song, G. Zhang and X. Guo, CrystEngComm
17 (37), 7160-7168 (2015).

[45] H. Wang, X. Yuan, Y. Wu, G. Zeng, X. Chen, L. Leng, Z. Wu, L. Jiang and H. Li, Journal of Hazardous Materials 286, 187-194 (2015).

[46] H. Wang, X. Yuan, Y. Wu, G. Zeng, X. Chen, L. Leng and H. Li, Applied Catalysis B: Environmental 174-175, 445-454 (2015).

[47] S. Rodriguez-Mozaz, S. Chamorro, E. Marti, B. Huerta, M. Gros, A. Sanchez-Melsio, C. M. Borrego, D. Barcelo and J. L. Balcazar, Water Res 69, 234-242 (2015).

[48] H. Wang, X. Yuan, Y. Wu, G. Zeng, H. Dong, X. Chen, L. Leng, Z. Wu and L. Peng, Applied Catalysis B: Environmental 186, 19-29 (2016).