Metal–Organic Layers for Electrocatalysis and Photocatalysis
Lingyun Cao and Cheng Wang*

ABSTRACT: Metal–organic layers (MOLs) are two-dimensional analogues of metal–organic frameworks (MOFs) with a high aspect ratio and thickness down to a monolayer. Active sites on MOLs are more accessible than those on MOFs thanks to the two-dimensional feature of MOLs, which allows easier chemical modification around the catalytic center. MOLs can also be assembled with other functional materials through surface anchoring sites that can facilitate charge/energy transport through the hybrid material. MOLs are thus quite suitable for interfacial catalysis like electrocatalysis and photocatalysis. In this outlook, we focus on representative progress of constructing unique interfacial sites on MOLs with designer paths for charge separation and energy transfer, as well as cooperative cavities for superior substrate adsorption and activation. We also discuss challenges and potentials in the future development of MOL catalysts and catalysts beyond MOLs.

Two-dimensional (2D) materials have attracted a lot of attention since the development of graphene. Metal–organic layers (MOLs) are 2D versions of metal–organic frameworks (MOFs). They are also known as coordination nanosheets (CONASHs), metal–organic framework nanosheets (MONs), and two-dimensional supramolecular polymers (2DSPs) in the literature. The MOLs discussed in this review are all ultrathin nanosheets of a monolayer or a few layers (less than five layers) in thickness with an aspect ratio over 100. The MOLs inherit features of both MOFs and 2D materials. For example, like other 2D materials, MOLs have active sites completely exposed on the external surface and thus highly accessible, as compared to active sites in the internal channels of MOFs. The MOLs were also much more mechanically flexible than the MOFs and easier to be dispersed in solvents for a range of applications. On the other hand, like MOFs, MOLs also have a regular network structure from alternately connected metal nodes (secondary building units = SBUs) and organic bridging ligands that can be rationally designed, leading to structural diversity and tunability. MOLs have emerged as a promising material for applications in separation, sensing, biomedicine, and catalysis.

MOLs can be prepared via two categories of strategies: top-down exfoliation and bottom-up assembly (Figure 1). The top-down method produces MOLs by selectively breaking interlayer bonding in bulk MOF crystals through external forces such as sonochemical exfoliation, solvent-induced exfoliation, freeze–thaw exfoliation, intercalation, or chemical exfoliation. These top-down methods are easy to scale up but difficult to obtain high quality materials of uniform thickness in many cases. These MOLs are quite suitable for scalable heterogeneous photocatalysis. The bottom-up assembly resembles MOF synthesis that uses a coordination reaction between the metal SBU and bridging ligands to construct networks but constrains its growth in the interlayer direction using either capping agents as modulators, surfactant-assisted synthesis, or interfacial preparation. MOLs produced by the bottom-up method can have regular morphology. Interfacial synthesis usually has issues of scale-up but may still be suitable for electrocatalysis as long as MOLs prepared on the interface can be transferred to electrode surface. Other methods based on modulator/surfactant need to consider the surface modification of prepared MOLs by these molecules, which may present mass transport barrier but may also provide a special microenvironment to tune the catalytical cavity. MOLs prepared by different methods have different unique properties that can be utilized in electrocatalysis and photocatalysis, highlighting the importance of target-oriented synthetic design.

The MOL structure can be characterized by a range of different methods (Figure 1), including electron microscopy (EM), scanning probe microscopy (SPM), powder X-ray diffraction (PXRD), X-ray absorption fine structure spectroscopy (XAFS), and atomic pair distribution function method (PDF). High-resolution EM methods can visualize the network of the SBUs, while SPM methods are quite suitable for

Received: August 26, 2020
Published: October 30, 2020
obtaining surface properties of nanosheets with a high resolution. Cryoelectron microscopy, which can slow down the electron beam damage of the ultrathin MOLs may help greatly to obtain atomic resolution images of these materials. Ultrathin nanosheets show distinct PXRD patterns that are different from 3D crystals, but the PXRD method usually cannot differentiate between the monolayer and nanosheets less than five layers in thickness. XAFS and PDF can be useful to differentiate between possible SBUs and/or to verify structures of active sites, but their interpretations must be evaluated with caution as usually a range of different structural models can fit in the same spectra.

As previous reviews of MOLs have provided detailed information on their synthesis,2,82,85,86 this outlook will focus on the progress of MOLs for electrocatalysis and photocatalysis, highlighting the structural basis for tuning their catalytic performance. We will then discuss the current challenges and emerging opportunities in this field.

■ CONSTRUCTING UNIQUE ACTIVE SITES ON MOLs

One major goal of MOL and MOF catalysis is to construct unique active sites that are unreachable from solution chemistry.

MOL and MOF catalysts bridge traditional homogeneous and heterogeneous catalysts but are also different from the two (Figure 2).

First, MOLs and MOFs have cavities that can interact with “transition state” species or “intermediates” in catalysis. This microenvironment mimics enzymes in which secondary interactions preconcentrate substrates and facilitate selective conversion. Secondary interaction between the substrate and a MOF cavity is also rich but still challenging to control. Surface modification of the MOL provides a new way to introduce the cooperative entities. As compared to modifying a MOF cavity, MOL surface modification does not have a space restriction and is thus more flexible.

Two examples from our group show the potential for MOL surface modification in photocatalysis and electrocatalysis.

(Figure 3). We prepared a MOL with a terpyridine (TPY) site on the ligand: \([\text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(HCO_2)_6(\text{TPY})_2]\). Postsynthetic functionalization of the TPY by ferrous salt gives a Fe center, which catalyzes photocatalytic aerobic oxidation of tetrahydrofuran (THF) to 2-hydroxy tetrahydrofuran (2-OH-THF, 43%) and butyrolactone (BTL, 57%). The MOL can then be surface-modified by attaching monocarboxylates with hydrophilic/hydrophobic tails on the SBUs, which tune the selectivity toward 2-OH-THF versus BTL. Hydrophilic...
modification with gluconate (GA) finally leads to 100% selectivity toward the more desired BTL product. This fine-tuning of product selectivity via the changing microenvironment does not require redesign of the active center and can be rationally implemented.

Using the same MOL with TPY site, we integrated cobalt-protoporphyrin (CoPP) onto the MOL by surface modification as the carboxylate group on CoPP can attach to the SBU (Figure 3). The surface-attached Co center cannot coordinate to TPY due to spatial isolation, but the two moieties can form a cooperative site that stabilizes a \([\text{TPYH}^-\cdot\text{O}_2\cdot\text{CoPP}]\) intermediate in electrochemical \(\text{CO}_2\) activation and reduction, leading to a high current density (1314 mA/mg Co, TOF = 0.4 s\(^{-1}\)) for \(\text{CO}\) production.\(^{35}\) This construction of cooperative sites from two moieties is challenging for homogeneous catalysts. MOLs thus provide an interesting supramolecular platform for building multifunctional sites.

Second, MOLs and MOFs can stabilize active metal centers with low coordination numbers or low numbers of strong coordination.\(^{36,42,44}\) In the Fe-TPY mentioned above, the Fe center on the MOL coordinates to the terpyridine moiety, while the other three coordination sites on Fe were occupied by labile solvent or counterions. Such a \([\text{Fe}^{II}(\text{TPY})]^{2+}\) moiety is not stable in the homogeneous system and tends to react with each other to form a \([\text{Fe}^{II}(\text{TPY})]^{2+}\) complex and free \(\text{Fe}^{II}\) ions. This stabilization effect by MOL is manifested in the turnover number (TON) of the aerobic oxidation of THF, which was 820 ± 30 for the Fe-functionalized MOL and was only 45 ± 2 for the \([\text{Fe}^{II}(\text{TPY})]^{2+}\) complex in solution.\(^{50}\)

Third, the active sites on MOLs and MOFs have relatively regular and clear structures. Other heterogeneous catalysts like supported metal on metal oxide usually have multiple local structures capable of catalytical conversion. Even homogeneous catalysts in solution can possibly form dimers to complicate their catalytic behavior. Site isolation on MOLs and MOFs stabilizes the single-metal site, making it possible to build catalysts of uniform sites. The structure certainty of organic binding sites as well as the availability of a crystal structure from X-ray diffraction adds having confidence in the structure models of catalytical centers in MOFs and MOLs.

However, this notion of a “clear structure” of MOL and MOF cannot be overinterpreted. Single crystal structure represents average positions of atoms in MOF, while catalysis happens locally on a specific site. For example, defects are often important in MOF catalysis but can hardly be captured by X-ray diffraction of MOFs. In addition, strong peaks on PXRD patterns may only reflect long-range order, while the local structure is more important for catalysis. As a result, partial loss of sharp PXRD peaks of MOFs may not necessarily correspond to destroying the structure of the local active site; on the other hand, retention of the PXRD pattern does not ensure a stable active site. Moreover, species captured by spectroscopic methods on the MOFs or MOLs were usually the stable species that may not necessarily turnover in catalytic cycle.

Besides, surface modifications of the MOLs were more challenging to characterize than structures in MOFs, as the single-crystal X-ray diffraction method can no longer be applied. Techniques developed for surface science such as SPM, sum-frequency generation (SFG) spectroscopy, and nano-IR can be useful to reveal the surface structure of MOLs, and aberration-corrected TEM has the potential to directly give the atomic image of the active center. These active sites on the MOLs were still much more manageable and tunable than those of many traditional heterogeneous catalysts.

Fourth, compared to active sites in MOFs, these sites on MOLs are more accessible as they were exposed on the external surface. This accessibility is critical for both electrocatalysis and photocatalysis. In electrocatalysis, these active sites can be in direct contact with the electrode, largely removing the electron conductivity requirement of the MOLs. In photocatalysis, as the excited state has a limited lifetime, and a more accessible excited state can greatly facilitate its utilization before decaying and being wasted. The accessibility of the active site also allows the approach of large organic substrates that can be challenging to accommodate in MOF channels. This key advantage of accessibility will be further exemplified in following sections.

Fifth, mechanically flexible and surface functionalized MOLs are suitable for assembling with a variety of other materials to obtain composite catalysts. The active sites can thus reside on the interface for interfacial catalysis. This is especially true for MOLs assembled on electrodes for electrocatalysis and on heterojunctions for efficient charge separation for photocatalysis.\(^{34,88,89}\)

Last but not least, the MOLs were still heterogeneous catalysts so that the active sites on MOLs can be easily isolated from the reaction mixture to shut down the reaction. The MOL catalysts can be recovered and reused, and more importantly they can be removed from the product by filtration to simplify workup of some organic transformations and avoid product contamination by heavy metals of the catalyst.\(^{43}\)

**FACILITATING ELECTRON TRANSFER OF MOLS FOR ELECTROCATALYSIS**

Although MOFs were widely investigated as electrocatalysts, in principle, their activities would be hindered by poor electrical conductivity of most MOFs. Chemical diversity of conductive MOFs is still limited.\(^{90}\) MOLs have monolayer thickness and can be assembled with a conductive electrode so that the active centers can be in direct contact with the electrode surface. Conductivity of the MOL skeleton is thus not necessary. The
mesh structure of the MOL still allows counterions and substrates to contact the electrode and the active sites.

There were MOFs constructed from redox active linkers that can conduct electrons or holes through subsequent redox reactions of the linkers in the framework, a so-called “hopping” mechanism. However, active sites on these MOFs can still be different from active sites on the MOLs in direct contact with the electrode. The latter can reside in the inner Helmholtz layer of the electrical double layer on the electrode and thus feel an electrical field in the catalysis, while the former only accepts conducted oxidation/reduction equivalents to react with the substrate in a regular redox reaction.

MOLs and MOFs have been widely investigated in a variety of electrocatalysis studies such as the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), overall water splitting, oxygen reduction reaction (ORR), carbon dioxide reduction (CO2RR), and electrocatalytic transformation of organic molecules. Some reported MOLs show comparable or even better performance than benchmark noble metal-based catalysts. There have been several reviews on the electrocatalytic performance of MOLs. Here we focus on how electron transfer is realized in these catalysts.

MOLs can be assembled with conductive materials. For example, we developed a method to grow MOLs around multiwalled carbon nanotubes (CNTs) with carboxylate on the surface for electrochemical oxidation of alcohols. Reprinted with permission from ref 34. Copyright 2018, American Chemical Society. Ni0.8Fe0.2(C12H6O4)(H2O)4 grown on nickel foam for efficient electrocatalytic water splitting. Reprinted with permission from ref 33. Copyright 2017, Springer Nature.

Figure 4. MOLs assembled on conductive substrates for electrocatalysis. (a) MOL-TEMPO on conductive multiwalled carbon nanotubes (CNTs) for electrochemical oxidation of alcohols. Reprinted with permission from ref 34. Copyright 2018, American Chemical Society. (b) Ni0.8Fe0.2(C12H6O4)(H2O)4 grown on nickel foam for efficient electrocatalytic water splitting. Reprinted with permission from ref 33. Copyright 2017, Springer Nature.

Besides electrocatalysis of organic molecules, the MOL assembly is also beneficial for electrocatalytic activation of small molecules, which usually involves a gas component either as a reactant or a product. For example, ORR and CO2RR have oxygen and CO2 in the gas phase, respectively, while HER and OER generate H2 and O2. A gas—liquid—solid triple-phase interface is critical in these types of catalysis. Control of the microstructure of the catalyst composite and tuning of hydrophilicity and hydrophobicity can have a huge effect on the overall catalytic performance. A 2D PcCu-O4–Co composed of copper phthalocyanine and Co2+, was loaded on CNTs to exhibit excellent electrocatalytic ORR activity (E1/2 = 0.83 V vs RHE, n = 3.93, and j1 = 5.3 mA·cm−2) in alkaline media. The mesoporous nest built from the CNTs certainly helped with the activity. It is also worth noting that this catalyst has a clear Co–O4 center as a catalytic site, as revealed by in situ Raman spectroscopy and density functional theory (DFT) calculations. Similarly, a bimetal NiFe-based MOF nanosheet assembled on nickel foam with hierarchical porosity demonstrates superior electrocatalytic performance toward OER and overall water splitting (Figure 4b).33

It is also beneficial to use conductive MOL in electrocatalysis. The π-conjugated metal bis(dithiolene) moieties can construct conductive MOLs that are electrocatalytically active. Monolayer THTNi (THT = 1,2,5,6,9,10-triphenylethene) synthesized by the Langmuir–Blodgett method is an active HER catalyst with an overpotential of 333 mV at 10 mA·cm−2. The NiS4 center on THTNi can function as a HER active site in a wide pH range. Further tuning electronic structures by ligand and metal substitution produced other active centers (MS4N4x−) with the HER activity following the order of CoS4N2 > CoN4 > CoS2 > NiS4, resulting from different H* adsorption and H2 desorption energies on these centers.

Some of the MOLs were not stable under electrocatalytic condition and can thus serve as a precursor to prepare the active ultrathin material. For example, the NiFe-based SURMOF was found to form NiFe-based oxy-hydroxide nanosheets while retaining coordinated ligands BDC-X (BDC = 1,4-benzenedicarboxylic acid, X = NH2, H, OCH3, and Br) as the active phase denoted as 1-X. These oxyhydroxides showed superior activity with a low overpotential of 220 mV at 10 mA·cm−2. In situ electrochemical transformation method was developed to prepare ultrathin metal oxide or hydroxide nanosheets with excellent electrocatalytic activity. A Fe doped 2D-Co–NS (Fe:2D-Co–NS@Ni) was prepared and used for OER, exhibiting an ultralow overpotential of 211 mV at 10 mA·cm−2. A bismuthene (Biene) of atomic thickness obtained from Bi-MOLs exhibited CO2RR activity with ~100% FE for formate.
MOFs have several key features that are beneficial for photocatalysis. First, as compared to MOFs, MOLs have fewer issues of light scattering, thanks to its ultrathin morphology and dispersibility in solvents.115 Second, the accessibility of active centers on MOLs is critical in photocatalysis as the excited state has a limited lifetime for singlet excited state and μs-ms for triplet excited state) during which the contact with substrate must happen to escape futile energy dissipation.38,39 Third, efficient energy transfer is critical for a range of photocatalysis, which will be detailed in the next section. Fourth, surface functionalization of a photoactive MOL can bring together two required components for photocatalysis: a chromophore for light harvesting and a catalytic center for chemical conversion.36,40,41,116 We focus on designing these synergistic entities on MOLs to facilitate electron transfer between the two in this section.36–41,60,65,115–123

A MOL from Lin’s group can serve as a typical example of hierarchically integrating photosensitizers ([Ru-(bpy)3]2+) and active centers (M(l-bpy)(CO)3X (M = Re, Mn)) in one skeleton for efficient photocatalysis (CO2RR) (Figure 5).37

Figure 5. Schematic showing the synthesis of Hf12-Ru-M (M = Re or Mn) via monocarboxylic acid exchange of Hf12-Ru and sunlight-driven CO2 reduction. Reprinted with permission from ref 37. Copyright 2018, American Chemical Society.

The MOL (Hf12-Ru) contains a Hf12(μ3-O)8(μ3-OH)8(μ5-OH)8(TFA)8 SBU (TFA = trifluoroacetate) and [Ru-(bpy)3]2+-based linear ligand L-Ru. All the capping TFA groups on the SBU can be replaced by M(l-bpy)(CO)3X moieties with carboxylate linkage on the bpy. The resultant multifunctional MOLs Hf12-Ru-M (M= Re or Mn) exhibit high activity for photocatalytic CO2 reduction to CO with a TON of 8613 which is about 70 times higher than that of a homogeneous control. The proximity of photosensitizers and catalytic centers in the MOL network facilitates electron transfer that initiates the photocatalysis.

OUTLOOK

The 2D morphology of MOLs together with regular and tunable structures is promising for electrocatalysis and photocatalysis. Though progress has been made during the past several years, there are still great challenges to overcome. Preparation of uniform MOLs in a reasonable scale is still difficult. The number of existing MOLs is too limited to meet the needs of designing various catalysts. Up to now, compared with more than 88 000 kinds of MOFs, the number of MOLs is no more than one percent of that of MOFs, and many of these MOLs were based on a similar skeleton structure.130 It is thus urgent to expand the diversity of these materials. This research demand can be combined with research of robotic combination chemistry and machine learning, which has...
been proven to be useful in expediting development of related materials.131

Stability of MOLs is another important aspect to consider. MOLs may undergo structural evolution under catalytic conditions. On the one hand, not only are more in situ spectroscopy and imaging studies needed to reveal the true active sites, but the durability of the catalyst also needs to be further verified through characterization of recovered sample, cycling experiments, and prolonged catalytic reaction. MOLs constructed from M–S and M–N coordination bonds are showing much improved chemical stability than those constructed from M–O bonds. Moreover, covalent organic frameworks (COFs) have seen rapid progress in the past few years, which can be much more stable than MOFs and MOLs. Development of monolayer of COFs is on the way, which can potentially change the landscape of 2D materials.

The high cost of MOLs/MOFs is often regarded as the Achilles’s heel for catalysis application. Practical use of a material is determined by the balance between its cost and the benefit it can bring. Targeting catalytic products of higher value can certainly improve the chance of developing a practical MOL catalyst. Even for commodity chemical synthesis, if the turnover frequency of the catalyst is extremely high, the operation can be insensitive to the cost of the catalysts, as already demonstrated by the success of noble metal catalysts in the Monsanto process to produce acetic acid. In situations where activity and/or selectivity are critical, catalysts of high costs can also have merits as exemplified by the expensive three-way catalysts for exhaust treatment on cars. We believe the cost of MOL should NOT be its final obstacle. The real challenge is to develop high performance MOL catalysts to meet the needs of catalytic applications.

Besides practical use, MOLs are also a useful platform for the academic study of catalysis. Designing model catalysts to gain mechanistic insight into complex reactions may lead to some discovery that is transferrable to more practical catalyst systems.

These challenges are also opportunities. MOLs as electrocatalysts and photocatalysts are becoming an exciting research field. We hope the progress of MOLs, combining knowledge of molecular catalysts and heterogeneous catalysts, can bring something new to the field.

■ AUTHOR INFORMATION

Corresponding Author
Cheng Wang – State Key Laboratory for Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering and Innovation Laboratory for Sciences and Technologies of Energy Materials of Fujian Province (IKKEM), Xiamen University, Xiamen 361005, China; orcid.org/0000-0002-7906-8061; Email: wangchengxmu@xmu.edu.cn

Author
Lingyun Cao – Innovation Laboratory for Sciences and Technologies of Energy Materials of Fujian Province (IKKEM) and State Key Laboratory for Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acscentsci.0c01150

Funding
The work is supported by funding from the Ministry of Science and Technology of China (2016YFA0200702), the National Natural Science Foundation of China (No. 21671162).

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. Science 2004, 306 (5696), 666–669.
(2) Cao, L.; Wang, T.; Wang, C. Synthetic Strategies for Constructing Two-Dimensional Metal-Organic Layers (MOLs): A Tutorial Review. Chin. J. Chem. 2018, 36 (8), 754–764.
(3) Sakamoto, R.; Takada, K.; Sun, X.; Pal, T.; Tsukamoto, T.; Phua, E. J. H.; Rapakousiou, A.; Hoshiko, K.; Nishihara, H. The
Film Electrical Conductivity and Fast Sensing Applications. CrystEngComm 2018, 20 (41), 6458–6471.

(21) Lu, W.; Wu, X. Ni-Mof Nanosheet Arrays: Efficient Non-Noble-Metal Electrocatalysts for Non-Enzymatic Monosaccharide Sensing. New J. Chem. 2018, 42 (5), 3180–3183.

(22) Hu, G.-B.; Xiong, C.-Y.; Liang, W.-B.; Tang, Y.; Yao, L.-Y.; Huang, W.; Luo, W.; Yuan, R.; Xiao, D.-R. Highly Stable Ru-Complex-Grafted 2D Metal-Organic Layer with Superior Electrochemiluminescent Efficiency as a Sensing Platform for Simple and Ultrasensitive Detection of Mucin 1. Biosens. Bioelectron. 2019, 135, 95–101.

(23) Liu, C.; Wang, T.; Ji, J.; Wang, C.; Wang, H.; Jin, P.; Zhou, W.; Jiang, J. The Effect of Pore Size and Layer Number of Metal-Porphyrin Coordination Nanosheets on Sensing DNA. J. Mater. Chem. C 2019, 7 (33), 10240–10246.

(24) Shi, M.-Y.; Xu, M.; Gu, Z.-Y. Copper-Based Two-Dimensional Metal-Organic Framework Nanosheets as Horseradish Peroxidase Mimics for Glucose Fluorescence Sensing. Anal. Chim. Acta 2019, 1079, 164–170.

(25) Liu, Q.; Li, X.; Wen, Y.; Xu, Q.; Wu, X. T.; Zhu, Q. L. Twofold Interverepenetrated 2d Mof Nanosheets Generated by an Instant in Situ Exfoliation Method: Morphology Control and Fluorescent Sensing. Adv. Mater. Interfaces 2020, 7 (16), 2000813.

(26) Lu, K.; He, C.; Lin, W. Nanoscale Metal–Organic Framework for Highly Effective Photodynamic Therapy of Resistant Head and Neck Cancer. J. Am. Chem. Soc. 2014, 136 (48), 16712–16715.

(27) Lan, G.; Ni, K.; Xu, R.; Lu, K.; Lin, Z.; Chan, C.; Lin, W. Nanoscale Metal–Organic Layers for Deeply Penetrating X-Ray-Induced Photodynamic Therapy. Angew. Chem., Int. Ed. 2017, 56 (40), 12102–12106.

(28) Lan, G.; Ni, K.; Veroneau, S. S.; Song, Y.; Lin, W. Nanoscale Metal-Organic Layers for Radiotherapy-Radiodynamic Therapy. J. Am. Chem. Soc. 2018, 140 (49), 16971–16975.

(29) Ni, K.; Lan, G.; Chan, C.; Duan, X.; Guo, N.; Veroneau, S. S.; Weichselbaum, R. R.; Lin, W. Ultragrain Metal-Organic Layered Radiotiotherapy-Radiodynamic Therapy. Matter 2019, 1 (5), 1331–1353.

(30) Wang, C.; Cao, F.; Ruan, Y.; Jia, C.; Zhen, W.; Jiang, X. Specific Generation of Singlet Oxygen through the Russell Mechanism in Hypoxic Tumors and Gsh Depletion by Cu-TCPP Nanosheets for Cancer Therapy. Angew. Chem., Int. Ed. 2019, 58 (29), 9846–9850.

(31) Zhu, W.; Yang, Y.; Jin, Q.; Cao, Y.; Tian, L.; Liu, J.; Dong, Z.; Liu, Z. Two-Dimensional Metal-Organic Framework as a Unique Theranostic Nano-Platform for Nuclear Imaging and Chemo-Photodynamic Cancer Therapy. Nano Res. 2019, 12 (6), 1307–1312.

(32) Zhao, S.; Wang, Y.; Dong, J.; He, C.-T.; Yin, H.; An, P.; Zhao, K.; Zhang, X.; Gao, C.; Zhang, L.; Lv, J.; Wang, J.; Zhang, J.; Khattak, A. M.; Ali Khan, N.; Wei, Z.; Zhang, J.; Liu, S.; Zhao, H.; Tang, Z. Ultralight Metal-Organic Framework Nanosheets for Electrocatalytic Oxygen Evolution. Nat. Energy 2016, 1 (12), 16184.

(33) Duan, J.; Chen, S.; Zhao, C. Ultrathin Metal-Organic Framework Array for Efficient Electrocatalytic Water Splitting. Nat. Commun. 2017, 8, 15341.

(34) Yang, L.; Cao, L.; Huang, R.; Hou, Z.-W.; Qian, X.-Y.; An, B.; Xu, H.-C.; Lin, W.; Wang, C. Two-Dimensional Metal-Organic Layers on Carbon Nanotubes to Overcome Conductivity Constraint in Electrocatalysis. ACS Appl. Mater. Interfaces 2018, 10 (42), 36290–36296.

(35) Guo, Y.; Shi, W.; Yang, H.; He, Q.; Zeng, Z.; Ye, J. Y.; He, X.; Huang, R.; Wang, C.; Lin, W. Cooperative Stabilization of the [Pyridinium-Co2-Co] Adduct on a Metal-Organic Layer Enhances Electrocatalytic CO2 Reduction. J. Am. Chem. Soc. 2019, 141 (44), 17875–17883.

(36) Shi, W.; Cao, L.; Zhang, H.; Zhou, X.; An, B.; Lin, Z.; Dai, R.; Li, J.; Wang, C.; Lin, W. Surface Modification of Two-Dimensional Metal-Organic Layers Creates Biomimetic Catalytic Microenvironments for Selective Oxidation. Angew. Chem., Int. Ed. 2017, 56 (33), 9704–9709.
Chem. Sci. 2017, 8 (5), 3955–3959.

2018, 14 (39), 12369–12373.

2018, 57 (17), 10490–10493.

2019, 141 (40), 15767–15772.

2014, 55 (16), 4962–4966.

Chem. Int. Ed. 2018, 57 (19), 3262.

Chem. Commun. 2017, 53 (20), 11198–11209.

Dalton Trans. 2013, 42 (43), 15267–15270.

Baldon, P. J.; Tomimakas, S.; Singh, P.; Saha Dasgupta, T.; Bithell, E. G.; Cheetham, A. K. Layered Structures and Nanosheets of Pyrimidinethiolate Coordination Polymers. Chem. - Eur. J. 2019, 25 (7), 5737–5744.

2015, 44 (7), 3417–3429.

2017, 23 (35), 8390–8394.

2015, 27 (45), 7372–7378.

2016, 12 (34), 4669–4674.

2017, 197, 217–220.
(104) Zhong, H.; Ghorbani-Askal, M.; Ly, K. H.; Zhang, J.; Ge, J.; Wang, M.; Liao, Z.; Makarov, D.; Zschech, E.; Brunner, E.; J. Am. Chem. Soc. 2020, 142 (4), 1746–1751.

(105) Kornienko, N.; Zhao, Y.; Kley, C. S.; Zhu, C.; Kim, D.; Lin, S.; Chang, C. J.; Yaghi, O. M.; Yang, P. Metal–Organic Frameworks for Electrocatalytic Reduction of Carbon Dioxide. J. Am. Chem. Soc. 2015, 137 (44), 14129–14135.

(106) Zhang, X.-D.; Hou, S.-Z.; Wu, J.-X.; Gu, Z.-Y. Two-Dimensional Metal-Organic Framework Nanosheets with Cobalt-Porphyrins for High-Performance CO2 Electroreduction. Chem. - Eur. J. 2020, 26 (7), 1604–1611.

(107) Zhong, H.; Ghorbani-Askal, M.; Ly, K. H.; Zhang, J.; Ge, J.; Wang, M.; Liao, Z.; Makarov, D.; Zschech, E.; Brunner, E.; Weidinger, I. M.; Zhang, J.; Krasheninnikov, A. V.; Kaskell, S.; Dong, R.; Feng, X. Synergetic Electroreduction of Carbon Dioxide to Liquid Fuel. Angew. Chem., Int. Ed. 2020, 59 (1), 1067–10682.

(108) Yang, L.; Ma, F.-X.; Xu, F.; Li, D.; Su, L.; Xu, H.-C.; Wang, C. Two-Dimensional Metal-Organic Layers for Electrochemical and Photocatalytic Electrocatalysis. Adv. Mater. 2020, 32 (35), 2005350–2005360.

(109) Xiao, Z.; Zou, L.; Pang, H.; Xu, Q. Synthesis of Micro/Nanoscale Metal-Organic Frameworks and Their Direct Electrochemical Applications. Chem. Soc. Rev. 2020, 49 (1), 301–311.

(110) Das, A.; Han, Z.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. Nickel Complexes for Robust Light-Driven and Electrocatalytic Hydrogen Production from Water. ACS Catal. 2015, 5 (3), 1397–1406.

(111) Mcnamara, W. R.; Han, Z.; Yin, C.-J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. Cobalt-Dithiolen Complexes for the Photocatalytic and Electrocatalytic Reduction of Protons in Aqueous Solutions. Proc. Natl. Acad. Sci. U. S. A. 2012, 109 (39), 15594–15599.

(112) Zhang, W.-D.; Yan, X.; Li, T.; Liu, Y.; Fu, Q.-T.; Gu, Z.-G. Metal-Organic Layer Derived Metal Hydroxide Nanosheets for Highly Efficient Oxygen Evolution. Chem. Commun. 2019, 55 (38), 5467–5470.

(113) Cao, C.; Ma, D. D.; Gu, J. F.; Xie, X.; Zeng, G.; Li, X.; Han, S. G.; Zhu, Q. L.; Wu, X. T.; Xu, Q. Metal–Organic Layers Leading to Atomically Thin Bismuthene for Efficient Carbon Dioxide Electroreduction to Liquid Fuel. Angew. Chem., Int. Ed. 2020, 59 (35), 15014–15020.

(114) Li, W.; Xue, S.; Watzele, S.; Hou, S.; Fichtner, J.; Semrau, A. L.; Zhou, L.; Welle, A.; Bandarenka, A. S.; Fischer, R. A. Advanced Biofunctional Oxygen Reduction and Evolution Electrocatalyst Derived from Surface-Mounted Metal–Organic Frameworks. Angew. Chem., Int. Ed. 2020, 59 (14), 5837–5843.

(115) Jiang, Z. W.; Zou, Y. C.; Zhao, T. T.; Zhen, S. J.; Li, Y. F.; Huang, C. Z. Controllable Synthesis of Porphyrin-Based 2D Nanoheterojunctions from Thickness- and Metal-Node-Dependent Photocatalytic Performance. Angew. Chem. Int. Ed. 2020, 59 (8), 3300–3306.

(116) Quan, Y.; Lan, G.; Fan, Y.; Shi, W.; You, E.; Lin, W. Metal–Organic Layers for Synergistic Lewis Acid and Photoredox Catalysis. J. Am. Chem. Soc. 2020, 142 (4), 1746–1751.

(117) Wang, Y.; Feng, L.; Pang, J.; Li, J.; Huang, N.; Day, G. S.; Cheng, L.; Drake, H. F.; Wang, Y.; Lollar, C.; Qin, J.; Gu, Z.; Lu, T.; Yuan, S.; Zhou, H.-C. Photosensitizer-Anchored 2D MoF Nanosheets as Highly Stable and Accessible Catalysts toward Artemisinin Production. Adv. Sci. 2019, 6 (11), 1802059.

(118) Hoo, D.; Lin, F.; Chen, S.; Ni, Y.; Wang, R.; Chen, H.; Duan, L.; Ji, Y.; Zhou, A.; Tong, L. Ruthenium Complex-Incorporated Two-Dimensional Metal-Organic Frameworks for Cocatalyst-Free Photocatalytic Proton Reduction from Water. Inorg. Chem. 2020, 59 (4), 2379–2386.

(119) Zuo, Q.; Liu, T.; Chen, C.; Ji, Y.; Gong, X.; Mai, Y.; Zhou, Y. Ultrathin Metal-Organic Framework Nanosheets with Ultrahigh Loading of Single Pt Atoms for Efficient Visible-Light-Driven Photocatalytic H2 Evolution. Angew. Chem., Int. Ed. 2019, 58 (30), 10198–10203.

(120) Xia, B.; Ran, J.; Chen, S.; Song, L.; Zhang, X.; Jing, L.; Qiao, S. Z. Two-Dimensional Metal-Organic Framework Accelerating Visible-Light-Driven H2 Production. Nanoscale 2019, 11 (17), 8304–8309.

(121) Ran, J.; Qu, J.; Zhang, H.; Wen, T.; Wang, H.; Chen, S.; Song, L.; Zhang, X.; Jing, L.; Zheng, R.; Qiao, S. Z. 2D Metal Organic Framework Nanosheet: A Universal Platform Promoting Highly Efficient Visible-Light-Induced Hydrogen Production. Adv. Energy Mater. 2019, 9 (11).

(122) Ye, L.; Gao, Y.; Cao, S.; Chen, H.; Yao, Y.; Hou, S.; Sun, L. Assembly of Highly Efficient Photocatalytic CO2 Conversion Systems with Ultrathin Two-Dimensional Metal-Organic Framework Nanosheets. Appl. Catal., B, 2018, 227, 54–60.

(123) Zhao, L.; Zhao, Z.; Li, Y.; Chu, X.; Li, Z.; Qu, Y.; Bai, L.; Jing, L. The Synthesis of Interface-Modulated Ultrathin Ni(II) MOF:g: C3N4 Heterojunctions as Efficient Photocatalysts for CO2 Reduction. Nanoscale 2020, 12 (18), 10010–10018.

(124) Webber, S. E. Photon-Harvesting Polymers. Chem. Rev. 1990, 90 (8), 1469–1482.

(125) Maza, W. A.; Padilla, R.; Morris, A. J. Concentration Dependent Dimensionality of Resonance Energy Transfer in a Postsynthetically Doped Morphologically Homologous Analogue of UiO-66 MOF with a Ruthenium(II) Polypyridyl Complex. J. Am. Chem. Soc. 2015, 137 (25), 8161–8168.

(126) Lee, C. Y.; Farha, O. K.; Hong, B. J.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. Light-Harvesting Metal–Organic Frameworks (MOFs): Efficient Strut-to-Strut Energy Transfer in Bodipy and Porphyrin-Based MOFs. J. Am. Chem. Soc. 2011, 133 (40), 15858–15861.

(127) Calzaferri, G.; Huber, S.; Maas, H.; Minkowski, C. Host–Guest Antenna Materials. Angew. Chem., Int. Ed. 2003, 42 (32), 3732–3758.

(128) Kent, C. A.; Liu, D.; Ma, L.; Papanikolas, J. M.; Meyer, T. J.; Lin, W. Light Harvesting in Microscale Metal–Organic Frameworks by Energy Migration and Interfacial Electron Transfer Quenching. J. Am. Chem. Soc. 2011, 133 (33), 12940–12943.

(129) Hu, X.; Chen, P.; Zhang, C.; Wang, Z.; Wang, C. Energy Transfer on a Two-Dimensional Antenna Enhances the Photocatalytic Activity of CO2 Reduction by Metal–Organic Layers. Chem. Commun. 2019, 55 (65), 9657–9660.

(130) Yilmaz, G.; Peh, S. B.; Zhao, D.; Ho, G. W. Atomic- and Molecular-Level Design of Functional Metal–Organic Frameworks (MOFs) and Derivatives for Energy and Environmental Applications. Adv. Sci. 2019, 6 (21), 1901129.

(131) Chen, P.; Tang, Z.; Zeng, Z.; Hu, X.; Xiao, L.; Liu, Y.; Qian, X.; Deng, C.; Huang, R.; Zhang, J.; Bi, Y.; Lin, R.; Zhou, Y.; Liao, H.; Zhou, D.; Wang, C.; Lin, W. Machine-Learning-Guided Morphology Engineering of Nanoscale Metal–Organic Frameworks. Matter 2020, 2 (6), 1651–1666.