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Review—2D Layered Metal Organic Framework Nanosheets as an Emerging Platform for Electrochemical Sensing

Varsha M. V. and Gomathi Nageswaran

Department of Chemistry, Indian Institute of Space Science and Technology, Thiruvananthapuram, Kerala 695547, India

E-mail: gomathi@iist.ac.in; sivakumar.gomathi@gmail.com

Abstract

Two dimensional layered metal-organic framework nanosheets, as a new class of porous crystalline materials have received extensive research attention owing to its intriguing chemistry and remarkable properties like ultrathin thickness, tunable structure, large specific surface area, high aspect ratio, accessible active sites, large pore volume etc. which leads to diverse applications. The unique properties originating from the combination of 2D structure and MOF provide opportunities for enhanced electrochemical activity due to the fast charge transfer and mass transport as well as increased number of surface active sites. In this review, we focus on the recent developments in 2D MOF nanosheet research with emphasize on synthesis and application. First, we summarize the different synthetic methods used for 2D MOF preparation using top-down and bottom-up approaches. In addition, the progress in the application of 2D MOF nanosheet as electrochemical sensing platform is explained in detail. Finally, the challenges and future perspectives for 2D MOF nanosheet research is presented.

This paper is part of the JES Focus Issue on 2D Layered Materials: From Fundamental Science to Applications.

Introduction

Two dimensional (2D) materials have gained intensive research interest since the isolation of monolayer of graphene for the first time in 2004 that create a breakthrough in material science and technology (1, 2). Other than graphene, a variety of novel 2D materials like transition metal dichalcogenides (TMDs) (3), hexagonal - boron nitride (h-BN) (4), graphitic - carbon nitride (g-CN) (5), layered double hydroxides (LDHs) (6), elemental 2D materials like borophene, phosphorene, silicene, germanene, antimonene etc. (4, 7) have also received much research attention. The dimensionality of a material is an important parameter in determining the properties of a material (8). When the interaction between layers is limited, the physical phenomena like charge transfer is highly restricted and the material exhibits excellent properties. 2D layered materials are endowed with versatile properties like high mechanical flexibility and optical transparency resulting from ultrathin atomic thickness which finds application in the field of flexible and transparent electronic and photoelectric devices (4, 9). The large traverse size makes it suitable for membrane for gas separation whereas the ultra-high specific surface area provides a number of accessible active sites for reaction, which improves the catalytic activity (10). Moreover, due to the unique electronic, mechanical and
optical properties, 2D materials are very significant in different fields of applications like catalysis, optoelectronics, energy storage/conversion and sensors (11-15).

Metal-organic frameworks (MOFs) are an emerging class of hybrid materials constructed from metal containing nodes (ions or clusters) and organic ligands (16). These are a class of highly ordered porous crystalline materials with exciting properties like large specific surface area (extending above 6000 m$^2$/g), ultrahigh porosity, tunable structure and pore size, unsaturated metal coordination site, controllable surface properties and varying morphologies (16-20). The extensive properties make MOFs significant in diverse fields of application like gas storage/separation (21, 22), energy storage/conversion (23-26), catalysis (27-30), sensors (31-33), drug delivery (34), biomedical imaging (35) etc. In addition, MOF-derived materials like functional carbon also find great potential in energy storage, catalysis and adsorption studies etc. (36-39). The history of MOF research started in 1990 by the works of Yaghi and co-workers in porous coordination polymers (40). Since then the field of material science witnessed an unparalleled growth in the number of research outcomes on MOF based materials. The unique aspect of MOFs is its topologically diverse crystal structures which can be tuned depending on research interest. MOFs can be designed to zero-dimensional nanoparticles, one-dimensional nanorods/wires, two-dimensional nanosheets and three-dimensional bulk crystals. A large number of research papers focus on the bulk 3D MOF crystals and 1D nanorods. However, 2D MOF nanosheets are increasingly explored in the recent years since the bulk MOF crystals do not completely satisfy the specific requirements for different applications.

Even though MOF possesses excellent properties, its limitations like low electrical conductivity and poor chemical stability hinder its application in the field of electrochemistry (41). 2D MOF nanosheets are an emerging member in the family of 2D materials, which combine the interesting properties of 2D materials and MOF. In order to generate 2D MOF nanosheets, the challenge of growth of MOF crystals lies in suppressing its growth along the vertical direction without affecting the other two lateral directions (42). The confinement of electrons in the 2D nanosheet promotes MOF for the fabrication of highly flexible and transparent electronic devices. The high surface area of 2D nanosheet results in the presence of a large number of exposed active sites on its surface compared to bulk MOF, which contain active sites mostly inside the pores and channels and improves the interaction between substrate species and active sites (42). This results in the enhancement of the reaction which can subsequently result in the improved performance for applications like sensing, catalysis and separation (43). Furthermore, 2D MOF nanosheets are more electrically conducting than bulk 3D MOF, which facilitate their application in electrochemistry (44). The application of 2D MOF nanosheets in the field of electrochemical sensing is less explored and is currently underway. Therefore, a comprehensive review covering the different aspects of 2D MOF nanosheets as a potential candidate for the development of novel sensing materials is absent.

In this review, we summarize the recent developments in the MOF nanosheet research with emphasis on its application in electrochemical sensing as demonstrated in scheme 1. Initially, different synthesis methods for the preparation of MOF nanosheets and its structural properties are discussed. The importance and different ways of functionalization of MOF nanosheets is explained giving examples of MOF based composites. The last section describes the application of 2D MOF nanosheets in the field of electrochemical sensing.
Scheme 1. Overview of synthesis methods and application of 2D MOF nanosheets

Synthesis of 2D MOF Nanosheets

In general, the synthesis of 2D MOF nanosheets can be broadly classified into two categories: top-down and bottom-up approaches. Top-down approach involves the exfoliation of bulk layered MOF by breaking the weak interlayer interactions (like van der Waals, hydrogen bonding etc.) (45, 46) within MOF, e.g. sonication exfoliation. This approach can potentially improve the yield of MOF. However, the vigorous exfoliation can often destroy the in plane coordination bond in MOF and generate small sized MOF nanosheets with low crystallinity. Bottom up approach involves the direct synthesis of MOF from its precursors by restricting the layer stacking along vertical direction. The restriction of growth of MOF along one direction with the other two lateral directions remain unaffected is a challenge. Moreover, it is a promising method to generate 2D layered MOF nanosheets through precise control of its synthesis process. In addition, non-layered 2D MOF nanosheets can also be synthesised by bottom up method (47). Herein, we summarize the two methods for 2D MOF synthesis with reported literatures.

Top-down synthesis

Pristine 3D bulk layered MOFs are formed by the stacking of 2D MOF layers via weak interactions (like π-π interaction between aromatic rings of organic ligands, van der Waals force and/or hydrogen bonding) along the vertical direction. In this method, the 3D layered MOFs are allowed to intercalate and exfoliate by means of chemical and physical methods to form single or few-layered 2D MOF nanosheets. The various top-down methods include sonication exfoliation, mechanical exfoliation, chemical exfoliation and Lithium intercalation.

In solvent exfoliation, solvents play two important roles; the exfoliation of layered MOF and to stabilize the as formed MOF nanosheets (i.e., to prevent the restacking of MOF layers). Therefore, the selection of suitable solvents is very crucial in determining the extent of exfoliation of layered bulk MOFs (47). Moreover, a mixture of solvents in specific ratio can also be used to achieve both the functions simultaneously (46). The role of solvent in
determining extent of exfoliation rate is not well understood till now, however it is believed that the surface energy of solvent is an important factor in determining the exfoliation of layered materials (48).

The first example of the isolation and characterization of coordination polymer flakes of one atom thickness under ambient conditions on a surface was reported in 2010 by Zamora and co-workers (49). They have synthesized black lustrous crystals of bulk $[\text{Cu}_2\text{Br(IN)}_2]_n$, (IZ-isonicotinato) by a hydrothermal redox reaction and the obtained compound ($10^{-10}$ mg/mL in water) undergoes sonication exfoliation to generate 2D $[\text{Cu}_2\text{Br(IN)}_2]_n$. The sonication treatment removed the interlayer n-n interactions between the aromatic isonicotinato ligands. The compound casted on a highly oriented pyrolytic graphite (HOPG) substrate shows a uniform and highly dense distribution of flakes with well-defined shapes and height of $5 \pm 0.15$ Å which is in good agreement with the theoretical value obtained for single atomic layer of $[\text{Cu}_2\text{Br(IN)}_2]_n$.

As another example, Li et al. reported the exfoliation of bulk Zn(BDC)(H$_2$O).DMF (or MOF-2) (where, BDC – 1,4-benzenedicarboxylic acid and DMF - N,N-Dimethylformamide) in acetone solvent (1 mg/mL) for 1 hr at room temperature to generate layered 2D MOF-2 nanosheets (50). The 2D MOF-2 obtained with the average thickness of 1.5 nm and lateral size of $200 \times 300$ nm$^2$ corresponds to two layers of MOF-2. However, it is also observed that after volatilizing the solvent, the exfoliated MOF-2 could restack in presence of amine which resulted in amine intercalation and reversible exchange of amines.

In 2016, Foster et al. reported the synthesis of a 2D layered MOF, Zn(1)DMF (1=2,5-Bis(3-methoxypropoxy)-1,4-benzenedicarboxylate), by incorporating weakly interacting chains of alkyl ether which assist formation of nanosheets by exfoliation of MOF layers (51). The layered MOF was sonicated in DMF (1 mg/ml) and centrifuged at 1500 rpm for 45 min. to obtain a clear suspension. They obtained the nanosheets with the thickness and lateral dimensions range from 5 to 30 nm and 100 to 500 nm respectively. The crystal structure of Zn(1)(DMF) predicts a single layer thickness of approx. 14.5 Å and a shorter interlayer spacing of approx. 9.4 Å (due to interpenetration of the 3-methoxypropoxy groups). This indicates a minimum thickness of the nanosheets corresponding to approximately five MOF layers.

Later in 2019, in order to understand the effect of the length of alkyl side chain on the nature of MOF nanosheets generated, Ashworth and co-workers synthesized a series of layered MOFs by liquid exfoliation in DMF and acetonitrile (MeCN) solvents (52). Copper paddle-wheeled MOFs with a range of organic ligands 2,5-bis(alkoxy)benzene-1,4-dicarboxylates ie., (O$_2$CC$_6$H$_2$(OR)$_2$CO$_2$, where R = methoxy to pentoxy) were synthesized. Thickness of the MOF nanosheets (MON) obtained by ultrasonication in MeCN was as low as 5 nm which corresponds to approximately five layers of MOF. In addition, a decrease in the average height of nanosheet of nearly 35-20 nm with increase in alkyl chain length was observed, which shows evidently the decrease in interlayer interactions with increase in the distance between layers. Furthermore, they have systematically studied the effect of surface functionalities as well as the importance of solvent – surface interaction on the extent of exfoliation of layered MOF by centrifugation of sonicated MOF suspensions at 1500 and 4500 rpm. It was observed that shorter alkyl chains resulted in higher concentration in suspension of MON in both the solvents.
Xu and co-workers developed the first luminescent 2D MOF nanosheets, \( \text{Ti}_2(\text{HDOBDC})_2(\text{H}_2\text{DOBDC}) \) (or NTU-9 nanosheet) (where, \( \text{H}_2\text{DOBDC} - 2,5\)-dihydroxyterephthalic acid) via top-down delamination by ultrasonicking the dried powder of NTU-9 in isopropanol (10 mg in 10 mL) for about 2 days at room temperature (53). The NTU-9-NS has a 2D layered morphology with thickness ranging from 15-50 nm which indicates that the exfoliated NTU-9-NS consist of multilayers. Even though sonication exfoliation is a widely adopted top-down method to synthesize 2D MOFs, the limitations like poor yield and energy consumption limit its application for large scale production of MOF.

There are other methods used to synthesize 2D layered MOF by the top down approach. Huang and co-workers designed a novel 3D pillared – layer type cobalt based MOF (3D-Co) by incorporating a catechol functionalized ligand (2,3-dihydroxy-1,4-benzenedicarboxylate ion, \( \text{H}_2\text{dhbdc}^{2-} \)) as the redox active pillar for oxygen evolution reaction (OER) catalysis (Fig. 1a&b) (54). The 3D Co electrocatalyst immersed in an O\(_2\) saturated, neutral electrolyte solution (water at pH =13) at 100 °C for 5 days undergo electrochemical exfoliation to form 2D periodically stacked MOF nanosheets. The mechanism of electrochemical exfoliation was analysed by mass spectrometry which reveals that the redox active pillar ligand, catechol, get selectively oxidized to lower their coordination ability between the layers and removed, maintaining the 2D layers intact.

Figure 1. a) Exfoliation of a pillared-layer MOF by selective pillar removal b) 3D stacked structure of the 2D layers along the \( b \)-axis in 2D-Co c) TEM and d&e) AFM images with corresponding height profile of 2D-Co-NS. Reproduced with permission from John Wiley and Sons (54)

Liu et al. synthesized a cobalt based layered MOF, denoted as Co-LMOF (Fig. 2), by a simple grinding method (55). The aqueous solutions of precursors were kept at room temperature for
several days to volatilize the solvent. The obtained red crystals were then ground for 2 h to obtain Co-LMOF with the size of the particles in the nanometer scale.

**Figure 2.** 2D molecular structure of Co–LMOF. Reproduced with permission from American Chemical Society (55)

Ogihara et al. reported the synthesis of a 2D layered intercalated MOF, 2,6-naphthalene dicarboxylate dilithium crystal denoted as (2,6-Naph(COOLi)2) (Fig. 3), by lithium-intercalation approach (56). The compound was synthesized from lithium hydroxide monohydrate and 2,6-naphthalenedicarboxylic acid under reflux condition in methanol. From XRD patterns, it was observed that (2,6-Naph(COOLi)2) consists of aromatic π-stacked naphthalene rings and tetrahedral LiO4 units of carboxylate group bind together which provide the electrochemical stability. The Li ions can increase the interlayer spacing and weaken the interaction between layers resulting in the exfoliation of bulk layered MOF.

**Figure 3.** Structure of 2,6-Naph(COOLi)2 before and after lithium-intercalation. Reproduced with permission from (56)
In summary, top-down methods are a simple and effective way to synthesize high quality crystalline 2D layered MOF. Despite the efficiency of the approach, top-down methods show certain limitations. The yield and rate of production of exfoliated MOF are very low for practical purposes (50). Furthermore, the stabilization of exfoliated 2D MOF is a challenge since there is great chance for restacking of 2D layers (46). Therefore, it is very important to explore other synthesis methods for the generation of 2D layered MOF.

**Bottom-up synthesis**

Complementary to the top-down method, bottom-up synthetic methods possess chemical tunability since it depends on the chemical reactions in a particular reaction condition. This approach involves the direct synthesis of single or few layer 2D MOF from metal ion and organic linkers. The important aspect of this method is the restriction of growth of MOF along the vertical direction i.e., prevent the stacking of MOF layers in one direction, without affecting the growth in other two lateral directions (42). There are three important ways to overcome the challenge of high surface energy of monolayers and generate 2D MOF layers by bottom-up assembly; chemical modification of the surface, tune the reaction conditions to allow the formation of high surface energy structures and perform synthesis at a confined 2D space. Different synthetic methods have been developed based on this strategy which involves interfacial synthesis, three-layer synthesis, surfactant-assisted synthesis, modulated synthesis and sonication synthesis.

**Interfacial synthesis**

Interfacial synthesis is one of the most widely used bottom-up approach which involves confining the chemical reactions between metal ion and organic ligands to an interfacial region. i.e. two dimensional space (interface) between two chemical phases (47). This method involves the dynamic arrangement of molecules in two dimension to generate MOFs with large lateral size and ultra-thin thickness. Depending on the interface involved, these are classified into liquid-liquid, air-liquid and gas-solid interfacial methods.

Liquid-liquid interfacial synthesis, involves the use of two immiscible solvents where metal dissolve in one solvent and ligand in the other. eg. water/ethyl acetate (57), water/dichloromethane (58) etc. MOF nanostructure generate in the interface of solvents based on a diffusion-mediated process. In 2014, Rodenas et al. synthesized Cu-BDC nanosheet by an interfacial synthesis involving copper nitrate and benzene-1,4-dicarboxylic acid (BDCA) as precursors (59). The bottom solution of organic ligand and top solution of Cu$^{2+}$, under static conditions, undergo diffusion into the intermediate spacer layer to form highly crystalline 2D MOF nanosheets. The synthesis involves the use of miscible solvents (DMF and CH$_3$CN) in appropriate ratio as different from the usual interfacial method. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies reveal that the nanosheet has a square lamellae structure with thickness 5-25 nm and lateral dimension 0.5 -4 µm. In addition, the change in reaction temperature can affect the growth kinetics of MOF and vary the thickness of nanosheet generated, as observed from SEM analysis. Wu et al. have developed a 2D copper based MOF (Cu-MOF) membrane which constitute a number of nanosheets by liquid-liquid interfacial approach (60). Copper acetate monohydrate
dissolved in water and tetrakis(4-carboxyphenyl)porphyrin (TCPP) dissolved in a mixture of 1-octanol and DMF (9 : 1) solvents kept in a vial for 3 days to form Cu-MOF membrane at the interface of solvents. FESEM images of Cu-MOF membrane clearly shows the presence of numerous nanosheets interconnected to each other which is considerably different from the bulk MOF with stacked layers. Sonication exfoliation of as prepared Cu-MOF membrane in water for 30 min. generated exfoliated Cu-MOF nanosheets. The decreased interlayer interaction in the 2D MOF membrane compared to layered bulk MOF made the exfoliation facile.

Liquid-air interfacial (such as water-air) synthesis involves the coordination reaction between metal and organic ligands at the liquid interface. Often, a small quantity of organic solvent is added on the water surface and once the solvent gets evaporated, the liquid-air interface will form. The well dispersion of a monolayer of organic ligand on the water surface allows the formation of ultra-thin or single layer 2D MOF nanosheets. Synthesis using the Langmuir-Blodgett (LB) vessel increase the yield of MOF nanosheet and the nucleation as well as the growth of MOF crystals can be controlled.

In a typical example, Makiura et al. developed a highly crystalline, large area single layer molecularly-thin 2D MOF nanosheet by interfacial growth at liquid-air surface in ambient conditions (61). The nanosheet were formed by the reaction between metalloporphyrin (PdTCPP) building units and aqueous solution of metal ion connectors (Cu(NO)_3·3H_2O) in the liquid-air interface of LB vessel (Fig. 4a). In order to optimize the parameters of MOF growth, in situ X-ray diffraction studies were carried out to observe the copper-mediated PdTCPP nanosheet formation at the interface (Fig. 4b). The presence of a number of sharp resolved peaks in the XRD profile indicate the formation of a highly crystalline large-scale MOF nanosheet structure.
In another example, Jiang and co-workers reported a porous, 2D MOF monolayer film with periodic hexagonal structure by the planar complexation reaction between Cu\(^{2+}\) and tri(β-diketone) ligands in a Langmuir-Blodgett (LB) trough (62). In this method, a 300 nm SiO\(_2\)/Si substrate was immersed in a LB vessel containing deionised water and a solution containing tri(β-diketone) in chloroform was carefully injected on the water surface. Once the organic solvent gets evaporated, a surface pressure of 0.8 mN m\(^{-1}\) applied and an aqueous solution of copper acetate was injected into the water phase. The single layer of MOF formed at the substrate was taken out, rinsed with chloroform and dried. The large area homogenous MOF film was obtained as monolayer with lateral size in the order of hundreds of µm with a smooth surface of ~ 0.7 nm thick.

Later, Gimenez et al. fabricated ultrathin, highly oriented and electrically conductive MOF film, Cu-CAT-1 (copper-catecholate 1) by LB method (63). The thin film formed at the liquid-air interface during the reaction between aqueous solution of Cu(OAc)\(_2\)·H\(_2\)O and HHTP (2,3,6,7,10,11-hexahydroxytriphenylene) in chloroform/methanol (3:1 v/v) on a PTFE substrate in a LB vessel is reported as the thinnest MOF film (10 nm) incorporating in MOF-based devices (Fig. 5).

In 2003, Dmitriev and co-workers reported the first gas/solid interfacial synthesis of MOF nanosheets under ultra-high vacuum (UHV) conditions (64). In this method, the metal atoms and organic ligands were deposited on a flat metal surface (like Cu (1 0 0), Au (1 1 1), Ag (1 0 0) etc.) kept in a UHV chamber of base pressure less than 5×10\(^{-10}\) mbar. Then, the substrate containing MOF components were annealed for certain time to initiate the coordination reaction between the MOF precursors to form 2D MOF nanosheets. The synthesised MOF nanosheets exhibit unique coordination modes.
In summary, interfacial synthesis is a simple and effective method for the synthesis of 2D MOF nanosheets. Generally, the synthesis of single or few-layer MOF nanosheets is more feasible by the liquid-air interface. Even though a number of 2D MOF nanosheets have been synthesized by this method, it possesses some limitations. This is not suitable for the high temperature synthesis of MOF nanosheets using metal clusters (65). In addition, the yield of MOF nanosheets is very low since it is determined by the size of interface, which limits its large scale synthesis.

**Solvo/hydrothermal synthesis**

The solvo/hydrothermal synthetic approach is an established and widely used method for the synthesis of ultrathin 2D MOF nanosheets. The synthesis is carried out in autoclaves or synthetic vials by heating in an oven. In some cases, the energy input can be given using continuous ultrasonic treatment for a long time which increases the molecular vibration and create localized hot points in the reaction mixture. This resulted in a hydrothermal environment for the synthesis of 2D MOF nanosheets. The different synthesis methods comes under this category are discussed further.

**Modulation method**

Modulator-assisted synthesis involves the use of small molecules called modulators (eg. pyridine, acetic acid, polyvinylpyrrolidone, trisodium citrate etc.) which control the nucleation and growth of MOF crystals along certain direction to form 2D MOF nanosheets. Modulators having the same functional groups as the organic ligand are chosen which selectively coordinate to the MOF nanosheet surface during its growth and restrict the stacking of layers which resulted in the anisotropic growth of MOF (66-68). In addition, the selection of appropriate modulators can generate MOF with different morphologies. eg. nanosheet, nanocube, nanorod etc.

Xu et al. developed a novel crystalline MOF thin film with highly oriented nanosheet structure, Cu-TCPP [TCPP= 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin], by a modular assembly method for the first time (69). The synthesis involves two steps: modularization and assembly. In modularization, highly crystalline MOF modules (i.e. Cu-TCPP nanosheets) with nanostructure are synthesized by a solvothermal reaction in DMF-ethanol solvent mixture. The second step involves the coordination of MOF modules into the MOF thin film via stamping process on a substrate (quartz) to generate thin film of controllable thickness (Fig. 6d). The average thickness of thin film obtained is ~ 15 nm corresponding to 33 layers of Cu-TCPP nanosheets (Fig. 6 a&b). TEM images reveal the smooth surface of nanosheets with uniform thickness. They have devised a method to prepare MOF thin films with controllable thickness on various substrates rapidly.
Later, Hu et al. synthesized a 2D layered MOF nanosheet, NUS-8(Zr/Hf) via heterogeneous modulated hydrothermal approach (70). The heterogeneous reaction was carried out in aqueous media at nearly 100 °C and 1 bar pressure which facilitate the fast nucleation and growth of MOF. A crystalline highly ordered domains in the internal fine structure of MOF nanosheets are reported (Fig. 7). In addition, the nanosheet morphology with thickness ~3 nm for NUS-8(Zr) and ~4 nm for NUS-8(Hf) correspond to approximately two or three layers.

In another example, He et al. for the first time, synthesized porous ultrathin zirconium-porphyrinic nanosheets by a one pot solvothermal reaction (71). By controlling the concentration of monocarboxylic acid (e.g., formic acid) which act as modulator help to obtain large single crystals of MOF with high yield (~85%). The obtained Zr-based MOF possess uniform nanosheet with thickness of 1.5 nm (Fig. 8b).
Interestingly, the concentration of modulator has a significant role on the morphology of MOF. As an example, the direct synthesis of 2D ultrathin cobalt based MOF nanosheets, Co$_2$(bim)$_4$ (bim=benzimidazole), by ammonia-modulated synthesis was reported in 2019 by Nian et al. (72). Ammonium hydroxide (NH$_4$OH), which acts as modulator, coordinatively binds with Co$^{2+}$ and restricts the growth of MOF along vertical direction by intercalation. Additionally, NH$_4$OH helps to deprotonate the ligand and boosts the nucleation as well as growth of MOF crystals. The investigation of the effect of NH$_4$OH/bim molar ratio on the morphology of MOF reveals that the morphology changes from bulk crystals to cubic shaped crystals with stacked layers and further to 2D nanosheets when the molar ratio changes from 0-2 and 2-4 respectively. The obtained MOF possesses few layered structure with average thickness of ~25 nm.

In recent years, the synthesis of bimetallic MOF nanosheets based on solvothermal reactions have also been reported. Li et al. synthesised various bimetallic MOF nanosheets, for the first time, by a solvothermal method in N,N-dimethylacetamide-water solvent mixture (Fig. 9 a) (73). They had prepared different Ni-M-MOF (where, M=Fe, Co, Al, Mn, Zn, Cd) nanosheets with ultrathin morphology. The solvent mixture played a significant role in regulating the morphology of MOF nanosheets. The nanosheets have a rough surface with a thickness of 1.67-2.58 nm as observed from the AFM images (Fig. 9 b).
Surfactant-assisted method

Surfactants are widely used in the synthesis of nanostructured materials to control the size of nanocrystals through its selective attachment on certain specific crystal planes. They perform two important functions in synthesis; reduce the surface energy of materials and modify or functionalize the nanostructured material surface (20). In MOF synthesis, surfactants are used to control the growth and nucleation of MOF and restrict the growth along vertical direction. This resulted in anisotropic growth of MOF from 3D bulk crystals to 2D nanosheets. MOF nanosheets have the tendency to restack or aggregate once it is formed due to its high surface energy. Therefore, synthesis of novel stable ultrathin 2D MOF nanosheets is a great challenge. Surfactants can selectively bind to the MOF surface and control its growth by weakening the interlayer interaction and preventing the stacking of MOF layers. Thus it stabilizes the as synthesized MOF nanosheet.

The synthesis of Zn-TCPP MOF nanosheet by Zhao and co-workers was reported for the first time based on this method (20). In Zn-TCPP, each layer contains TCPP ligand coordinated to four secondary building units of zinc paddle-wheel metal nodes i.e. Zn$_2$(COO)$_4$. The layered sheets are stacked in AB pattern (Fig. 10 a). In FTIR data, a shift in peak position from 1662 cm$^{-1}$ to 1619 cm$^{-1}$ for the carbonyl group of PVP (surfactant) was observed after the addition of Zn metal precursor (Fig. 10 c). The sharp peak corresponding to Zn-CO indicates the strong interaction between Zn$^{2+}$ and carbonyl group in PVP. This suggests that PVP gets selectively attached to the Zn$_2$(COO)$_4$ metal nodes and controls the anisotropic growth of MOF to form nanosheets. Zn-TCPP nanosheet has an ultrathin morphology (Fig. 10 b) and thickness of 7.6 ± 2.6 nm with nearly 8 ± 3 layers. Applying this as a general method, they have synthesized a series of 2D MOF nanosheets of M-TCPP (M=Cu, Cd, Co) with thickness sub–10 nm.
Figure 10. a) Schematic of the traditional synthesis and surfactant-assisted synthesis of MOF b) TEM image of a single Zn-TCPP nanosheet c) FTIR spectra of synthesized nanosheet (20). Reproduced with permission from John Wiley and Sons

Later, the same research group have developed a series of 2D bimetallic MOF nanosheets, M-TCPP(Fe) where M = Co, Cu and Zn, with ultrathin nature based on a bio-inspired design for the first time using PVP surfactant (Fig. 11) (74). TCPP(Fe), an iron-porphyrin derivative which acts as a heme like ligand was used for the synthesis of M-TCPP(Fe). The crystal structure consists of one TCPP(Fe) ligand connected to four M$_2$(COO)$_4$ paddle wheel metal nodes. The thickness of Co-TCPP(Fe) is observed to be 5.6 ± 1.8 nm. The synthesized M-TCPP(Fe) nanosheets possess heme protein like activity and can be used as a biomimetic enzyme for various applications.

Figure 11. Schematic representation of synthesis of 2D Co-TCPP(Fe) nanosheets by surfactant-assisted method (74). Reproduced with permission from John Wiley and Sons

Recently, Zheng et al. developed an ultrathin 2D cobalt-MOF nanosheet by a surfactant assisted controllable on-pot hydrothermal method using PVP as surfactant (75). The synthesized 2D Co$_2$(OH)$_3$BDC nanosheet possesses an ultrathin morphology with thickness ~ 2 nm. Other than PVP, there are other surfactants used for the synthesis of MOF which include sodium dodecylbenzene sulfonate (76), cetyl trimethyl ammonium bromide (CTAB) (77) etc.
In conclusion, the 2D MOF nanosheets are endowed with highly accessible surface for functionalization, large number of exposed active sites, increased aspect ratio and provision for surface engineering methods. The different synthesis methods employed for MOF nanosheet preparation does not affect or deteriorate the structure of bulk MOF. As a result, 2D MOF nanosheets retain the chemical and physical properties of bulk MOF that offer advantages of diverse application fields.

Applications of 2D layered MOF

Owing to the combined characteristics of 2D nanostructure and MOF, the 2D layered MOF nanosheets possess unique properties and used in a wide range of applications. In recent decades, MOFs have been widely employed in the field of electrochemistry for catalysis, energy conversion and storage and sensing. The advantages of large specific surface area, tunable structure, porous network, accessible metal active sites and facile mass transport pathway offer advantages towards electrochemical applications. However, the low electrical conductivity and poor stability in certain electrolytes hinder its application as an electrode material. The development of unique nanostructured 2D layered MOF with hierarchical porous features have received great interest in recent years. In this section, we will briefly discuss the recent developments of 2D MOF for electrochemical sensing.

Electrochemical Sensing

The development of novel 2D nanostructured layered MOF materials for the fabrication of electrochemical sensors is a nascent field which receives increasing research attention. 2D MOF nanosheet has the potential to be used as a sensing platform due to its intriguing properties. The ultrathin nature of nanosheet along with the high specific surface area provides considerable affinity for adsorption of analytes. The tunability of its structure by changing the precursors offers versatile properties suitable for specific application. Moreover, electrochemically active 2D MOF can be developed by using redox active metal nodes or organic ligands.

Wang et al. in 2016, developed a novel electrochemical sensing platform for detecting H$_2$O$_2$ based on a series of 2D bimetallic MOF nanosheet denoted as M-TCPP(Fe) (M=Co, Zn, Cu) (74). Thin films of Co-TCPP(Fe) nanosheet on glassy carbon electrode [(Co-TCPP(Fe))$_n$/GC] were fabricated by Langmuir-Schafer method. Among the different modified electrodes, (Co-TCPP(Fe))$_5$/GC exhibited the highest catalytic activity for the detection of H$_2$O$_2$ with high sensitivity of 35.4 µA cm$^{-2}$ mM$^{-1}$ and low detection limit of 0.15 × 10$^{-6}$ M. Additionally, the sensor material shows high reproducibility, superior stability and a linear increase in reduction current in the concentration range of 0.4×10$^{-6}$ - 50×10$^{-6}$ M. Further, the proposed sensor was employed for the real time analysis of H$_2$O$_2$ secreted by living cells which finds application in the diagnosis of breast cancer.

In a typical example, Su et al. reported the synthesis of a 2D composite material of zirconium based MOF nanosheet embedded with gold (Au) nanoclusters (denoted as AuNCs@521-MOF) and its application as electrochemical aptasensor for sensing cocaine (78). The Zr-based MOF possesses strong affinity towards phosphoric group by Zr-O-P bond formation. Along with this, the high specific surface area of 2D nanosheet as well as excellent electrochemical activity of Au NCs together make the composite a highly promising sensing platform with good
electrochemical activity and strong bio affinity for analyte. The modified electrode anchored with aptamer strands (Apt/AuNCs@521-MOF/AE) selectively binds to the cocaine. The proposed sensor shows wide linear detection range (0.001-1.0 ng mL\(^{-1}\)), very low detection limit (0.44 pg mL\(^{-1}\)) and excellent selectivity.

In 2017, Shu et al. had prepared a nanocomposite based on Ni and NiO nanoparticle decorated MOF nanosheet by the calcination of Ni-MOF in suitable condition (79). The obtained nanocomposite Ni-MOF/Ni/NiO/C immobilized on GC and applied for non-enzymatic detection of glucose. The sensor exhibited higher electrocatalytic activity towards glucose oxidation and shows satisfactory results when employed for real time monitoring of glucose in human serum. The amperometric study reveals higher sensitivity of the modified electrode due to the increased absorption as well as activation of glucose on the electrode surface. The lower limit of detection (0.8 µM), higher sensitivity (367.45 mA/M/cm\(^2\)) and wide linear concentration range (4-5664 µM) shows that the developed material is promising for electroanalytical applications. Further, the material exhibited excellent sensitivity towards H\(_2\)O\(_2\) detection.

In 2018, Zhao et al. had prepared a novel porphyrin based small crystals of MOF, 2D Zn-TCPP MOF nanodisk via top down modulation method using 4,4'-biphenyldicarboxylic acid (BPDC) as modulator (80). The as formed Zn-TCPP complex has a 4-coordinate structure which in presence of nitrite (donor molecule) becomes a 5-coordinate structure due to the selective binding of nitrite with the axial ligand of MOF. The Zn-TCPP(BP) nanodisk deposited on FTO substrate was applied for the electrocatalytic oxidation as well as detection of nitrite. The modified electrode shows excellent sensitivity (158.1 µA/mM/cm\(^2\)) due to the independent distribution of porphyrin in framework which increase the number of accessible active sites for nitrite ions. In addition, the lower detection limit (0.26 µM) can be ascribed to the sandwich structure of nanodisk as well as small size of crystals which resulted in large area of contact between material and nitrite ions. Furthermore, the real time analysis of nitrite in different water samples shows good recovery of 93-109 % with high accuracy.

In the same year, Shao et al. fabricated a novel Faraday cage-type electrochemiluminescence (ECL) sensor based on multi-functionalized 2D nanomaterials by extending the outer Helmholtz plane (OHP) of the biosensor for the simultaneous determination of miRNA-141 and miRNA-21 (81). The constructed sensor display excellent sensitivity for miRNA-141 and miRNA-21 with linear range of 1 fM to 10 pM and detection limit of 0.3 fM. Moreover, the fabricated miRNA assay shows high selectivity and sensitivity for real time analysis in human serum. Thus the potential-resolved ECL biosensor is proved to be a feasible tool for multiple targets detection of microRNAs in clinical diagnosis.

In 2019, Zou et al. had constructed a non-enzymatic glucose sensor based on a series of bimetallic ultrathin Ni/Co MOF nanosheets with different metal ratios (82). The synergistic effect between Ni and Co plays a significant role in the enhancement of electrochemical activity of the sensor material. In addition, the electrocatalytic activity can be enhanced by tuning the metal ratio. It was observed that Ni/Co-MOF nanosheet with the Co-Ni ratio of 2:1 shows the highest electrochemical performance towards glucose sensing. The increased bonding interaction between metal sites and O atom in glucose facilitates the electron transfer between MOF nanosheet and analyte which resulted in the high affinity of sensor material towards glucose. Furthermore, due to the synergistic effect, the electrochemical oxidation of

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glucose gets promoted at comparatively low applied potential. From EIS analysis, it was observed that all the prepared MOF nanosheets have low charge transfer resistance (< 50 Ω) which is attributed to the ultrathin structure with large area that facilitates the direct contact of analyte with electrode surface. The prepared sensor displays wide linear range (0.1 µM-1.4 mM), low detection limit (0.047 µM), extremely high sensitivity (2086.7 µA/mM/cm²) and satisfactory results for real sample analysis with 90.1 % accuracy.

In another example, Zhao et al. developed a composite material consisting of 2D Cu-TCPP MOF and platelet ordered mesoporous carbon termed as Cu-TCPP/pOMC-3 by solvothermal reaction (83). The incorporation of pOMC into the 2D MOF enhance the conductivity, weaken MOF layer accumulation on electrode and the metal sites of MOF get exposed. The composite inherits the advantages of both MOF as well as POMC; the higher catalytic activity of CuTCPP combined with large surface area of 2D nanostructure endows effective close contact with the analyte (hydroxylamine). This enhances the charge transfer as well as loading capability which in turn increase the concentration of hydroxylamine and electrocatalytic process. The sensor shows outstanding electrochemical performance with a very wide linear range for hydroxylamine having two segments (5.8-733.8 µM and 733.8-2933.8 µM) and excellent sensitivity (10.18 µA/µM) towards chlorogenic acid detection.

Li et al. synthesised a novel vertically standing 2D NiCo-MOF nanosheets on the surface of nanoporous gold by hydrothermal method and used for non-enzymatic glucose sensing (84). The obtained nanosheet has parallelogram shape with average thickness 65 nm where the nanopores direct the vertical growth of 2D MOF by preventing the stacking of NiCo-MOF array. The vertical orientation has the advantages of higher number of accessible active sites which triggers electron and mass transport. The synergistic effect between Ni and Co as well as the strong interaction of Ni, Co and N in MOF nanosheet provides the material superior electrochemical activity. The performance of the sensor includes broad linear range of 1 µM-8 mM, good sensitivity (0.6844 mA/mM/cm²), lower limit of detection (0.29 µM) and high reproducibility and stability.

Recently, Liu et al. had prepared a series of 2D ultrathin MOF nanosheets (Co-MOF, Ni-MOF, NiCo-MOF) incorporating electrochemically exfoliated graphene (EG) (85). The modified sensor material (M-MOF/EG) was employed for glucose sensing which shows the lowest oxidation potential for glucose at 0.2 V, wide linear range of 1-3330 µM and detection limit (0.58µM) for Co-MOF/EG/GCE. The exfoliated graphene sheets act as a filler that synergise and improves the analytical performance and structure of MOF.

In another recent work, Dong et al. fabricated a non-enzymatic electrochemical immunosensor for calprotectin (CALP) based on 2D ultrathin Cu-TCPP(Fe) nanosheet functionalized with PtNi nanospheres (86). The electrocatalytic activity as well as conductivity of bimetallic MOF increased when nanospheres get attached to its surface. This functionalization provides scope for antibody immobilization through modified active sites. The sandwich type electrochemical immunoassay possesses high sensitivity for CALP detection with detection limit 137.7 fg/mL and broad linear range of 200 fg/mL – 50 ng/mL. The use of PtNi@Cu-TCPP(Fe) can be extended for applications in clinical diagnosis of different biomarkers.

Other than the above mentioned works, there are some other reports on the development of novel 2D MOF materials for the application of electrochemical sensing. Reports of research on 2D MOF based electrochemical sensors first published in 2016. From then, this area is
receiving increasing research attention. The literatures of 2D MOF nanosheet based electrochemical sensors are summarized in table 1.

| Material            | Analyte                  | LDR       | LOD      | Sensitivity (µA/mM/cm²) | Ref. |
|---------------------|--------------------------|-----------|----------|-------------------------|------|
| 521-MOF             | Mucin 1                  | 0.001-0.5 ng/mL | 0.12pg/mL | -                       | (87) |
| Ni-MOF/NF           | Glucose                  | 0.04 – 2 mM | 85 nM    | -                       | (88) |
| Cu-TCPP/MWCNT       | H₂O₂                     | 0.001-8.159 mM | 0.70 µM | 157                     | (89) |
| Ni-MOF/Hemin        | H₂O₂                     | 1 µM-0.4mM | 0.2 µM   | 38                      | (90) |
| PXa/Au/Cu-TCPP      | Dopamine                 | 5-125 µM  | 1.0 µM   | -                       | (91) |
| AuCu/PPy/Cu-TCPP    | H₂O₂                     | 7.10µM-24.10 | 6.67 nM | 35.0                    | (92) |
| AgNPs/Cu-TCPP       | H₂O₂                     | 3.7 µM-5.8 mM | 1.2 µM | 2.16                    | (93) |
| Co-MOF              | Glucose                  | 0.5-8065.5 µM | 0.25 µM | 219.67                  | (94) |
| Co-MOF/NF           | Glucose                  | 0.01 mM-3 mM | 1.3 nM   | 10886                   | (95) |
| Ni-MOF              | Hydrazine hydrate        | 0.5-8000 µM | 0.23 µM | 2412                    | (96) |
| Cu-BTC/g-C3N4       | glyphosate               | 1.0×10⁻¹²- | 1.3×10⁻¹³ | -                       | (97) |
| Ni-BDC              | Glucose                  | 0.01-0.8mM | 6.68 µM | 636                     | (98) |
| BPNSs/TH/Cu-MOF     | miR3123                  | 2 pM-2 µM | 0.3 pM   | -                       | (99) |

BPNSs-black phosphorous nanosheets, TH-thionine, BDC-benzenedicarboxylic acid, g-C3N4-graphitic carbon nitride, NF-nickel foam, PPy-polypyrrole, PXa-poly(xanthurenic acid), TCPP-tetrakis(4-carboxyphenyl)porphyrin, 521-MOF-zirconium based MOF
2D MOF nanosheet vs. other 2D materials and its stability

The extremely high surface area of 2D MOF nanosheet (> 6000 m²/g) compared to other state-of-the-art 2D materials like graphene, transition metal dichalcogenides etc. along with its ultrathin nature facilitates direct contact of analyte with the electrode surface and leads to high affinity for analyte absorption. Due to the large specific surface area, the 2D MOF based electrodes have increased number of accessible active sites which enhances the electron and mass transport between MOF and analyte species and subsequently leads to higher sensitivity of the 2D MOF modified electrode. Another unique characteristic of MOF is its structure tenability which allows control over the modification of structure for specific analytes. In the case of a bimetallic MOF nanosheet, the synergistic effect between the metal atoms enhances the electrochemical activity of the modified electrode. i.e. by tuning the metal ratio, catalytic activity can be changed. However, the low electric conductivity of 2D MOF relative to other 2D nanomaterials remains as a challenge. This can be solved, to an extent, by developing 2D MOF nanosheet based composites which combines the advantages of large surface area of MOF as well as high catalytic activity of metal nanoparticles, metal oxides etc. The enhanced charge transfer between composite modified electrode and analyte leads to high sensitivity.

From the extensive study of 2D MOF nanosheets, it can be understood that, these materials possess a wide range of exciting properties as well as some limitations like poor conductivity and low stability which specifically hinder its application for practical purposes. The chemical as well as mechanical stability of a material is an important aspect to be considered in the fabrication of electronic devices. In the case of 2D MOF nanosheet, the synthetic methods need to be modified in such a way that it should result in high yield of homogeneously dispersed uniform MOF nanosheets with good structural stability. The fabrication and application of 2D MOF nanosheet based functional (opto)electronic devices face challenges with respect to the stability of MOF nanosheet incorporated which adversely affects the device performance.

The stability of MOF nanosheet can be tuned in a number of ways. The exfoliated nanosheet obtained during top-down synthesis (sonication exfoliation) from bulk layered MOF has the tendency to restack via weak interaction. The use of solvents having similar surface energy as that of exfoliated nanosheet and the use of a mixture of solvents are the promising ways to prevent stacking (46). In a mixture of solvents, one solvent facilitates exfoliation whereas the other solvent helps to stabilise the exfoliated nanosheet. Another approach to tune the stability is to insert rigid pillars into the flexible framework of MOF structure. The 2D pillared MOFs have superior stability compared to bulk MOF due to the strong coordination bond between layers where the pillar ligands are intercalated (100). 2D MOF nanosheets with high thermodynamic stability could be obtained by this method which can be used for selective gas adsorption studies. Furthermore, formation of 2D MOF nanosheet based composites or hybrid structures with other 2D nanomaterials opens new pathways to generate stable 2D MOF nanostructures for diverse applications.

Conclusion and Future Perspectives

In summary, the review gives an overview of the important developments in the synthesis as well as electrochemical sensing applications of 2D layered MOF nanosheets. The different synthetic strategies for 2D MOF preparation under the classification of top-down and bottom-
up approaches have been introduced briefly. Among the different top-down methods, exfoliation of 3D bulk MOF by sonication is widely used. Even though top-down approach has several advantages, the drawbacks of poor yield as well as stability of exfoliated sheets hinder its widespread application for practical purposes. The combination of two methods as well as use of solvents having the similar surface energy as that of MOF can improve the yield and prevent the restacking of layers respectively. Compared to top-down approach, bottom-up synthesis involves direct synthesis of MOF from its precursors which provides opportunities for controllable growth of MOF by tuning the precursor composition and synthetic conditions. However, the development of other facile synthetic methods for high quality 2D MOF is significant.

The review summarizes almost all the 2D MOF nanosheet materials developed so far for electrochemical sensing application. The use of 2D MOF as electrode material for sensing is still in the infancy stage. There are several challenges that need to be addressed for successful fabrication of MOF based sensors. 

i) The relative low stability of 2D MOF in acidic as well as basic aqueous electrolyte solutions.

ii) The poor electrical conductivity of pristine MOF when employed as electrode modifier that reduce sensitivity.

iii) The development of semi-conductive 2D MOF nanosheet based opto(electronic) devices as they are very rare due to the limited number of high quality MOF nanosheet.

iv) Understanding on the underlying mechanism for 2D MOF based electronic devices.

v) Develop novel 2D MOF based flexible devices since MOF have features of flexibility and film forming capacity.

vi) Based on theoretical calculations, predict the electronic properties of 2D MOF and design its synthesis prior to its assembly in devices.

The structure optimization of a material along with understanding of its working mechanism in devices is essential for increasing the performance of an electronic device. 2D MOF nanosheets are fabricated into devices including amperometric, luminescent, capacitive and chemiresistive sensors. They have been considered as a potential candidate in functional (opto)electronic devices. Furthermore, the development of stable conductive MOF materials with excellent electrochemical performance is very significant. The formation of novel hybrid nanostructures combining 2D MOF with other 2D materials further widen their properties and applications. In addition, synthesis of 2D MOF nanosheet based composites with metal nanoparticles, metal clusters, oxides, sulphides etc. need to be explored well. Moreover, efficient synthetic methods for the scalable synthesis of high quality MOF nanosheets with tunable structure and functions in order to fabricate devices need to be developed.
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