Chapter 10

Graphene-Metal Organic Framework Composite Based Electrochemical Sensors for Toxic Chemicals

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Abstract

Metal organic frameworks (MOFs) are a class of porous materials designed by coordination chemistry between metal ions and secondary organic building units (linkers). They emerged as an extensive class of crystalline materials with higher porosity than other framework materials like zeolites, activated carbon and metal-complex hydrides, respectively. Besides, they have high thermal stability, well-organized structure, low density, large internal surface area, ease in synthesis and broad-spectrum properties which makes them suitable for diverse applications. On the other hand, bulky structure of MOFs having some limitations like poor solubility, lacking electronic conductance and surface to volume ratio is minimal. To fulfill the above shortcoming is to introduce properties of other active materials like carbon nanostructure, metal oxide, metal nanoparticles, graphene carbon nitrite so on. Among the different composite materials especially carbon-based nanocomposite like graphene oxide (GO) and its derivatives have gained much attention because GO exhibiting 2D amphiphilic contains huge hydroxyl, epoxy and carboxylic acid functional groups on its conjugated planes.
The co-existence of aromatic sp² feature and oxygen functionalities allow GO in wide bonding interactions. Due to the solubility, sheet with basal like structure of GO can easily functionalized with other active materials. The obtained composite materials could enhance the optical, electrical, thermal and mechanical properties and can then be utilized for electrocatalytic applications. This chapter deals with the introduction of MOF with different synthetic methods and their characterization. Then these composite materials are utilized for electrochemical determination of toxic components including heavy metals, toxic anions, pesticides, aromatic nitro compounds, phenolic compounds and toxic solvents. The described MOF with graphene-based composites are well-known electrocatalyst for determination of toxic compounds.

Keywords
Metal-Organic Frameworks, Graphene Oxide, Electrocatalyst, Electrochemical Sensors, Toxic Components, Aromatic Nitro Compounds

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1. Introduction

In recent years, researchers have made great progress in constructing new chemical design structures from zero-dimensional (0D) to 3D by assembling the different building units [1]. A well-defined framework assembly of building units to the architectures have been attained by diverse connecting points like weak $\pi$-$\pi$ stacking and strong covalent bond interactions [1,2]. The metal-organic frameworks (MOFs) could be obtained via coordination between metal ions and secondary building units (SBUs) [3,4] (Figure 1A). The SBUs are different functionalities, i.e. bi-dentate to poly-dentate carboxylate functional groups have been utilized to develop a new type of organic frameworks [2-5]. The structural designs of MOFs are based on selection of metal ions and organic linkers to form 3D network frameworks (Figure 1B).

![Figure 1. Scheme showing the formation of MOF (A) and MOFs with different dimensionalities (B).](image)

In addition to that, organic linkers can also be important for connecting units in the assembly of MOF structures [6]. It is difficult to predict the MOF structure on the basis of the organic linkers and metal ions used [5,6]. MOFs are specific kinds of flexible porous crystalline materials with different dimensionalities and various topologies could be obtain on the basis of metal ion geometry and secondary organic building units [2-6]. The MOFs can be categorized based on the guest species and also depending upon the structural dimensionality. Figure 1B displays the different dimensional organic
frameworks with respect to metal ion and ligands. In 1D frameworks, the coordination bonds are spread over the polymer in one direction and possible cavities are accommodated with small sized molecules [7-9]. In 2D frameworks, a single type layers are superimposed through either edge to edge or staggered type of stacking where weak interactions exist between the layers [7,8]. The modifications of ligand which constitute the layers can control the way of stacking and functionality [8]. In 3D MOFs, frameworks are highly porous and stable due to the coordination bonds spread in three directions. The 3D pillared layers and grids are found in most of the MOFs [2-8].

1.1 Synthesis of MOF

1.1.1 Solvothermal and hydrothermal synthesis of MOFs

In the synthesis of MOFs, the building units and synthetic routes must be carefully selected based on the requirement of framework structures. The MOFs were synthesized via hydrothermal and solvothermal, microwave, sonochemical and electrochemical methods (Figure 2). The solvothermal and hydrothermal methods are one of the important synthetic methods for highly crystalline organic framework structures [10-13]. Generally, organic solvents such as N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), N-methylpyrrolidine (NMP) and dimethyl sulfoxide (DMSO) were frequently used in the synthesis of solvothermal method [12,13]. The solvothermal synthesis of different organic and inorganic framework materials often takes several hours and requires heating based on the solvents (80-180ºC) within a sealed vessel. The pressure inside the sealed vessel is very important, which may affect the yield significantly. These synthetic methods are similar with only difference being the utilization of solvent. Recently, much effort has been devoted to the hydrothermal synthesis of different metallic organic frameworks in green (water used as solvent) and facile ways. The varieties of synthetic reports are available in the literature for solvothermal and hydrothermal for metal organic frameworks [10-13].

1.1.2 Microwave synthesis of MOFs

Microwave synthesis method has been extensively used for quick and rapid synthesis of highly porous crystalline under protic conditions [14]. Besides fast crystallization and tuning the structures, potential advantages of this technique include phase selectivity, particle size distribution, and controlling the growth of the structures [15]. Commercial microwave equipment provides adjustable power outputs and has a fiber optic temperature and pressure controller. In microwave synthesis, a substance mixture in a suitable solvent and then transferred into a Teflon linked vessel, sealed and placed in the microwave unit, and heated for the appropriate time at an optimized temperature [16]. In
this technique, where an applied electric field is coupled with the permanent dipole moment of the molecules in synthesis medium inducing molecular rotations, results in rapid heating of the liquid phase [15,16]. The MW synthetic technique has been used for the synthesis of diverse metal organic frameworks [14-16].

Figure 2. Scheme showing the different synthetic routes of MOFs and its properties.

1.1.3 Sonochemical synthesis of MOFs

A Sonochemical method is one of the easiest and effective synthesis routes for crystalline MOF. An accelerated nucleation can also achieve a reduce in crystallization time and significantly smaller particles size than other conventional methods [17,18]. The mixture of substance solution was introduced into a reactor fitted to a sonicator bath with variable power output without external cooling. Initially, formation and collapse of bubbles was formed in the solution after sonication, termed acoustic cavitation, produces very high local temperatures and pressures, and results in producing fine crystallites [19]. These are some common example for the synthesis of highly crystalline MOFs sonochemically [17-19].

1.1.4 Electrochemical synthesis of MOFs

An electrochemical synthesis is classified as two main categories like anodic and cathodic electro deposition [20-22]. The anodic electrochemical synthesis metal ions continuously supplied through anodic dissolution as a metal source instead of metal salts, which react with the dissolved organic linkers and a conducting salt in the reaction
medium [23]. The metal deposition on the cathode is avoided by employing protic solvents, but in the process H₂ is generated. The electrochemical route is also possible to run a continuous process to obtain a higher solids content compared to conventional batch reactions [24]. The first electrochemical synthesis of Cu-MOF using bulk copper plates are arranged as the anodes in an electrochemical cell with the 1,3,5-benzene tricarboxylic acid (H₃BTC) dissolved in MeOH as solvent and a copper cathode. During a period of 150 min at 12-19 V and 1.3 A, a greenish blue precipitate was formed. After activation, a dark blue colored powder (octahedral crystals in 0.5 to 5 μm) having surface area of 1,820 m²/g was obtained. There are some common examples for synthesis of different MOFs by electrodeposition [20-24].

1.1.5 Mechanochemical synthesis of MOFs

Mechanical synthesis is a green technology and breakage of intra-molecular bonds followed by a chemical transformation taking place [25,26]. Highly porous nature of MOF synthesis by mechanochemical was reported first in 2006. Mechanochemical reactions can takes place at room temperature under solvent-free conditions, which is especially advantageous when organic solvents can be avoided [26]. Quantitative yields of small MOF particles can be obtained in short reaction times, normally in the range of 10-60 min. In many occasions, metal oxides were found to be preferred than metal salts as a starting material, which results in water as the only side product [26]. The addition of small amounts of solvents in liquid-assisted grinding can lead to acceleration of mechanochemical reactions due to an increase of mobility of the reactants on the molecular level [25-27]. Already many analytical reports are available for the synthesis of MOFs via mechanochemical method [25-27].

1.2 Composition of MOFs

In recent years, MOF has received arousing interest due to their high surface area, pore volume and excellent thermal conductivities [1-5]. The synthesized MOFs are potentially utilized in various fields such as catalysis, gas storage, adsorption, drug delivery, chemical and electrochemical sensors [1-5,7,9,12]. But limitation of MOF is its poor electrical conductivity due to the presence of non-conducting organic ligands and huge molecular weight of the framework structures [28]. To fulfill the above limitation, MOF was prepared as composites with different functional materials. The combination of MOFs with active functional materials has been offered recently to enhance the functional activity than MOF alone [7]. The result of the composite material provides fabrication protocols for high-performance composites with sophisticated architectures [7]. The hybrid composites are combination of two or more distinct constituent materials with properties noticeably different from those of the individual components [3,7].
composite materials shows good structural flexibility, high porosity with ordered crystalline structures and various kinds of functional properties like unique optical, electrical, magnetic and catalytic [3-6]. Therefore, new physical and chemical properties and enhanced the electro catalytic performance than individual components [8]. Consequently, the remarkable features of composites resulting from the synergistic combination of both MOF and other active components make them suitable for a wide range of applications [3-8]. To date, MOF composites have been successfully made with active species, including metal nanoparticles (NPs), metal oxides (MOx), quantum dots (QDs), polyoxometalates (POMs), polymers, graphene, carbon based materials [3,5,6-8] Figure 3.

1.2.1 MOF with carbon-based composites

MOFs with carbon-based composites are most important because it possesses various allotropes like graphite, fullerenes, nanotubes and diamond, micro textures with different degrees of graphitization, dimensionality from 0D to 3D [3,7,8]. As the most promising candidates for functional applications especially graphene and carbon nanotubes (CNTs), are gaining increasing attention owing to their outstanding properties of in-plane graphite with a high surface area [29]. Graphene is a monolayer of carbon atoms arranged in a 2D honeycomb lattice and can be seen as an individual atomic plane pulled out of bulk graphite [7]. Graphene oxide (GO) is a graphene derivative derived from the oxidative exfoliation of graphite, which is solution-dispersible and can act as the precursor of
graphene after reduction [29,30]. On the other hand, CNTs are well-ordered, high aspect ratio allotropes of carbon. The two main variants, single-walled carbon nanotubes (SWCNTs, diameters of 0.4 to 2 nm) and multi-walled carbon nanotubes (MWCNTs, diameters of 2 to 100 nm), both possess a high tensile strength, ultra-light weight, and excellent chemical and thermal stability [29-31]. The exceptionally mechanical, electrical and thermal properties of graphene commend them as valuable nanostructured fillers in MOF composites [29,31]. The MOF composites, which combines graphene based materials with functional inorganic materials resulting in a combination of the individual properties, is even more predestined for applications concerning sustainable energy and environment [3,7,8,29,31]. To date, numerous MOF–nanocarbon composites have been successfully made with graphene oxide intensively explored for diverse applications.

1.2.2 Electrochemical sensor using MOFs

Electrochemical sensors is one of the important analytical detection tool and they can provide high sensitivity and selectivity with relatively inexpensive equipment compared to conventional techniques. The MOF with graphene oxide composites have been extensively used for electrochemical sensing applications (Figure 4). The redox and catalytically active sites were introduced through the use of active metal ions or ligands in MOFs, thereby detection of metal ions and nitro compounds was achieved [31,32]. The MOFs were rarely used for conductance-based sensing applications because of their poor electrical conductance [28]. At present, the research on pure MOFs in electrochemical sensors is still shortcoming. Therefore, researchers prepared composites with graphene oxide to be used to detect nitro compounds, toxic anions, hazards compounds and environmental pollutants [32]. The superior electrocatalytic activity of the MOF with graphene oxide composites make them feasible for various sensing applications. The presence of MOF with graphene based composites on electrode surface facilitates the sensitivity, selectivity, anti-interference activity and lowers the limit of detection (LOD). Further, the oxidation/reduction potentials of the analytes can favorably shift to the lower values during electrochemical sensing studies.

This chapter concludes the electrocatalytic activity of MOF-graphene based composites reported for electrochemical sensing of toxic chemicals, environmental pollutants, toxic metal ions, nitro aromatic compounds and toxic solvents. It also discusses various advantages of the MOF with graphene based composites for electrochemical sensing applications. The MOF with graphene oxide based composites have been applied for electrocatalytic application of various environmentally important analytes like toxic metal ions, nitroaromatic compounds, phenolic isomers. Information is given in this
chapter for the synthesis, properties and applications of MOF with graphene based composites as electrocatalyst for sensing approaches.

Figure 4. Scheme showing the MOF with composites for electrochemical application.

2. MOFs based Electrochemical sensors

The metal organic framework structures have been extensively used for electrochemical sensing applications. The redox and catalytically active sites were introduced through the use of active metal ions or ligands in MOFs, thereby electrochemical detection of toxic metal ions, nitro compounds and hazards compounds [33-50]. In recent years, MOFs were rarely used for conductivity-based sensing applications because most of the MOFs are less conductivity. However, the application of MOFs in non-enzymatic electrochemical sensors has aroused widespread concern in recent years. Cui et al. reported the synthesis of 4,4'-bipyridine based Cu-MOF [Cu(bpy)(H₂O)₂(BF₄)₂(bpy)] by deposition. The synthesized Cu-MOF was modified on carbon paste electrode (CPE) and then utilized for 2,4-Dichlorophenol, an exhibited a wide linear range concentration from 4 to 100 × 10⁻⁶ M with LOD 1.1 × 10⁻⁶ M [33]. Song et al. reported the bimetallic CoNi-MOF using mixed organic linkers 4-(1H-tetrazol-5-yl)benzoic acid (H₅TZB) and 2,4,6-tri(4-pyridyl)-1,3,5-triazine (TPT). The bimetallic-MOF was utilized for trace level determination of hazardous compounds deoxynivalenol (DON) and salbutamol (SAL) by
EIS. The sensor showed linear wide range from 1 to $500 \times 10^{-12}$ mL$^{-1}$ with LOD $0.05 \times 10^{-12}$ mL$^{-1}$ [34].

Li et al. demonstrated the sensing of heavy metal ions ($\text{Cd}^{2+}$) using the Mg-MOF from 3,3'-((pyridine-2,5-diyl)dibenzoic acid and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ by reflux. The obtained sensor showed wide-linear range from 0 to 60 μg L$^{-1}$ by SWASV with LOD 0.12 ppb (S/N = 3) [35]. Sohail et al. displayed the water stable Zn-MOF and then utilized for oxidation of hydrazine. It showed wide linear range from 20 to $350 \times 10^{-3}$ M ($R^2 = 0.9922$) for hydrazine by linear sweep LSV with LOD of $2 \times 10^{-3}$ M ($n = 3$) was observed [36]. Wang et al. reported simultaneously detection of multiple heavy metal ion pollutants ($\text{Cd}^{2+}$, $\text{Pb}^{2+}$ and $\text{Cu}^{2+}$) using ferrocenecarboxylic acid functionalized Zr-MOF (Fc-NH$_2$-UiO-66). The LODs of the ratiometric sensor were estimated to be $8.5 \times 10^{-9}$ M for $\text{Cd}^{2+}$, $0.6 \times 10^{-9}$ M for $\text{Pb}^{2+}$ and $0.8 \times 10^{-9}$ M for $\text{Cu}^{2+}$, respectively [37]. Zhang et al. reported the Ce-MOF modified with cationic surfactant of cetyltrimethylammonium bromide (CTAB). The CTAB/Ce-MOF was modified on GCE and then utilized for Bisphenol A by DPV and wide linear range from 0.005 to $50 \times 10^{-6}$ M with LOD $2.0 \times 10^{-9}$ M (S/N=3) [38].

Ji et al. reported the Cu based MOF and then utilized for Sunset yellow (SY) and tartrazine (TZ). It showed wide linear range concentration from 0.3 to 50 nM and 1.0 to 100 nM for SY and TZ with LOD 0.05 and 0.14 nM [39]. Wang et al. reported the burkholderia cepacia lipase (BCL) modified with Cu-MOF nanofibers for hazards pesticides. It showed good sensitivity for wide range from 0.1 to $38 \times 10^{-6}$ M with LOD $0.067 \times 10^{-6}$ M for methyl parathion. Finally it showed good selectivity and practical application was demonstrated in residues in vegetable samples [40]. Figure 5 shows the various electrochemical sensors using MOF modified electrodes. Roushani et al. synthesized the Zn based MOF and then utilized for hazards $\text{Cd}^{2+}$. The obtained sensor based on interaction between $\text{Cd}^{2+}$ and –N complexation by soft-soft interaction. The obtained sensor exhibited wide range concentration from 0.7 to 120 with LOD 0.2 μg L$^{-1}$ [41].

Zhang et al. reported the core–shell nanostructured composite of Fe(III)-MOF with mesoporous Fe$_3$O$_4@mC$. The Fe-MOF@mFe$_3$O$_4@mC$ showed an excellent electrochemical activity towards $\text{Pb}^{2+}$ and $\text{As}^{3+}$, good water stability and high specific surface area. The wide range concentration from 0.01 to $10 \times 10^{-9}$ M with LOD 2.27 and $6.73 \times 10^{-12}$ M toward detecting $\text{Pb}^{2+}$ and $\text{As}^{3+}$ was achieved [44]. Guo et al. reported the amino-functionalized Ni(II)-MOFs using 2-aminobenzenedicarboxylic acid as an organic linker by one-pot hydrothermal method. The prepared Ni-MOFs were found to be an effective material for selective detection of microgram levels of $\text{Pb}^{2+}$ in an aqueous solution performed by SWASV [45]. Kung et al. demonstrated the porphyrin based Zr-MOF (MOF-525) thin films are grown on conducting glass substrates by solvothermal
approach. The modified glass substrate was utilized for determination of nitrite by AMP and wide linear range concentration from 20 to $800 \times 10^{-6}$ M with LOD $2.1 \times 10^{-6}$ M, respectively [46]. Prathap et al. reported the highly porous ZIF-8 in an aqueous solution at room temperature and then utilized for electrochemical sensing of trinitrotoluene (TNT). The interaction between the electron-deficient aromatic core of TNT and the electron-rich ZIF-8 is considered to favor the formation of donor–acceptor electron-transfer mechanism, and the electron conductivity of ZIF-8 facilitates the effective reduction of TNT. The sensor performance is highly linear, with very low LOD $346 \times 10^{-12}$ M [47].

Su et al. reported the Zr-MOF (MOF-525) with crystal sizes ranging from 100 to 700 nm were synthesized by adjusting the content of benzoic acid by solvothermal synthetic process. The synthesized crystals showed similar surface area of 2500 m$^2$/g with a unique pore size of 1.85 nm. The MOF thin films were applied for electrocatalytic nitrite oxidation and great detection limit of $0.72 \times 10^{-6}$ M with high sensitivity of 40.6 $\mu$A/mM-cm$^2$ [48]. Bao et al. reported the ultrathin Ni-MOF nanobelts, $[\text{Ni}_{20}(\text{C}_5\text{H}_6\text{O}_4)_2\text{H}_2\text{O}_{8}]$ 40 H$_2$O (Ni-MIL77), have been exploited for non-enzymatic urea sensor. Ni-

MOF ultrathin nanobelts exhibit a high sensitivity of 118.77 mA mM\(^{-1}\) cm\(^{2}\), wide linear range of 0.01 to 7.0 \times 10^{-3}\) M with LOD 2.23 \times 10^{-3}\) M (S/N = 3) [49]. Arul et al. synthesized the Ni-MOF capped with polyvinyl pyrrolidone (PVP) using 2-aminomethyl-1,4-benzene dicarboxylic acid (NH\(_2\)-1,4-BDC) by solvothermal method. The Ni-MOF-PVP/GCE exhibited a wide range concentration from 0.2 \times 10^{-6}\) M to 1 \times 10^{-3}\) M with the LOD of 97 \times 10^{-9}\) M (S/N = 3) was achieved by AMP [50] Figure 6 shows the various electrochemical sensing of toxic metal, nitrocompounds using MOFs modified electrodes. The electrocatalytic performance of the MOFs fabricated electrode was utilized towards the detection of toxic chemicals and environmental pollutants is summarized in Table 1 [33-50]. The use of one-component MOFs as electrode material in electrochemical sensors often results in wide linear ranges, a low sensitivity, and poor stability due to their less electron conductivity with poor mechanical properties. Hence, MOFs with graphene based composites to improve the sensitivity, stability and linear range detection.

Table 1. Comparison of performance of the MOFs fabricated electrochemical sensors towards the detection of toxic ions and environmental pollutants.

<table>
<thead>
<tr>
<th>Sensing material</th>
<th>Technique</th>
<th>Analytes</th>
<th>Linear range (M)</th>
<th>Detection limit (M)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-MOF</td>
<td>DPV</td>
<td>DCP</td>
<td>$4 - 100 \times 10^{-6}$</td>
<td>$1.1 \times 10^{-6}$</td>
<td>33</td>
</tr>
<tr>
<td>CoNi-MOF</td>
<td>EIS</td>
<td>DON &amp; SAL</td>
<td>$1 - 500 \times 10^{-2} \text{M L}^{-1}$</td>
<td>$0.05 \times 10^{-12} \text{M L}^{-1}$</td>
<td>34</td>
</tr>
<tr>
<td>Mg-MOF</td>
<td>SWASV</td>
<td>Cd$^{2+}$</td>
<td>$0 - 60 \times \mu \text{g L}^{-1}$</td>
<td>$0.12 \text{ppb}$</td>
<td>35</td>
</tr>
<tr>
<td>Zn-MOF</td>
<td>DPV</td>
<td>Hydrazine</td>
<td>$20 - 350 \times 10^{-3}$</td>
<td>$2 \times 10^{-3}$</td>
<td>36</td>
</tr>
<tr>
<td>Zr-MOF</td>
<td>DPV</td>
<td>Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$</td>
<td>$1 \times 10^{-9} - 2 \times 10^{-6}$</td>
<td>$8.5, 0.6, 0.8 \times 10^{-9}$</td>
<td>37</td>
</tr>
<tr>
<td>CTAB-Ce-MOF</td>
<td>DPV</td>
<td>BSA</td>
<td>$0.005 - 50 \times 10^{-6}$</td>
<td>$2.0 \times 10^{-9}$</td>
<td>38</td>
</tr>
<tr>
<td>Cu-MOF</td>
<td>DPV</td>
<td>SY &amp; TZ</td>
<td>$0.3 - 50, 1.0 - 100 \times 10^{-9}$</td>
<td>$0.05 &amp; 0.14 \times 10^{-9}$</td>
<td>39</td>
</tr>
<tr>
<td>Cu-MOF</td>
<td>SWASV</td>
<td>MP</td>
<td>$0.1 - 38 \times 10^{-6}$</td>
<td>$0.067 \times 10^{-6}$</td>
<td>40</td>
</tr>
<tr>
<td>Zn-MOF</td>
<td>DPV</td>
<td>Cd$^{2+}$</td>
<td>$0.7 - 120 \times \mu \text{g L}^{-1}$</td>
<td>$0.2 \times \mu \text{g L}^{-1}$</td>
<td>41</td>
</tr>
<tr>
<td>Yb-MOF</td>
<td>SWASV</td>
<td>Cd$^{2+}$ &amp; Pb$^{2+}$</td>
<td>$0.1 - 1.0 \times 10^{-6}$</td>
<td>$0.10 \times 10^{-9}$</td>
<td>42</td>
</tr>
<tr>
<td>Zn-MOF</td>
<td>DPV</td>
<td>TCAA</td>
<td>$0.02 - 1 \times 10^{-6}$</td>
<td>$1.89 \times 10^{-6}$</td>
<td>43</td>
</tr>
<tr>
<td>Fe-MOF</td>
<td>EIS</td>
<td>Pb$^{2+}$ &amp; As$^{3+}$</td>
<td>$0.01 - 10 \times 10^{-9}$</td>
<td>$2.27, 6.73 \times 10^{-12}$</td>
<td>44</td>
</tr>
<tr>
<td>MOF-525</td>
<td>Amp</td>
<td>Nitrite</td>
<td>$20 - 800 \times 10^{-6}$</td>
<td>$2.1 \times 10^{-6}$</td>
<td>46</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>DPV</td>
<td>TNT</td>
<td>$0.4 - 460 \times 10^{-9}$</td>
<td>$346 \times 10^{-12}$</td>
<td>47</td>
</tr>
<tr>
<td>Zr-MOF</td>
<td>CV</td>
<td>Nitrite</td>
<td>$10 - 800 \times 10^{-6}$</td>
<td>$0.72 \times 10^{-6}$</td>
<td>48</td>
</tr>
<tr>
<td>Ni-MOF</td>
<td>DPV</td>
<td>Urea</td>
<td>$0.01 - 7 \times 10^{-3}$</td>
<td>$2.23 \times 10^{-3}$</td>
<td>49</td>
</tr>
<tr>
<td>Ni-MOF-PVP</td>
<td>DPV</td>
<td>NB</td>
<td>$0.2 \times 10^{-6} - 1 \times 10^{-3}$</td>
<td>$97 \times 10^{-9}$</td>
<td>50</td>
</tr>
</tbody>
</table>

2,4 dichlorophenol (DCP); deoxynivalenol (DON); Salbutamol (SAL); Bisphenol A (BSA); Sunset yellow (SY) and Tartrazine (TZ); Methylparathion (MP); Trinitro-toluidine (TNT); Nitrobenzene (NB), Square-Wave Anodic Stripping Voltammetry (SWASV); Electrochemical impedance spectroscopy (EIS), Differential pulse voltammetry (DPV).

3. MOFs with graphene-based composites

In recent years, an increasing interest has been focused on metal nanoparticles (MNPs), graphene and graphene-based nanocomposites [7,8]. Owing to high mechanical strength and chemical stability as well as electrical resistivity, graphene and its counterparts including graphene oxide (GO) and nitrogen doped graphene (N-GO) etc. It has been demonstrated as an excellent catalyst for various nano-architectures and catalyst specific
reactions. Hybridization with different nanocrystals including noble metals, metal oxide and sulfides and metal coordination compounds has proven effective for enhanced physicochemical properties and chemical functions, ranging from gas adsorption, catalysis, photovoltaic device and sensors [1,3-5,7,8,29]. Li et al. reported the novel synthesis of Cu-MOFs with electrochemically reduced graphene oxide (ERGO) based composites. The Cu-MOFs/ERGO composites displayed significantly enhanced electrocatalytic activity towards BSA. It showed wide linear range concentration from $0.02 - 90 \times 10^{-6}$ M with LOD of $6.7 \times 10^{-9}$ M (S/N=3) by DPV [51].

Saraf et al. reported the simple ultra-sonication of slow diffusion driven Cu-MOF with chemically rGO. The synergistic effects between Cu-MOF with rGO Nano-sheets exhibited high charge storage efficiency (685.33 F.g$^{-1}$ at 1.6 A.g$^{-1}$) and high energy (137.066 W h kg$^{-1}$). Additionally, electrode modified with Cu-MOF/rGO hybrid performs exceptionally towards the electrochemical detection of nitrite in a wide linear range from $3 - 40000 \times 10^{-3}$ M ($R^2 = 0.99911$), with a notable LOD of $33 \times 10^{-9}$ M and a high sensitivity of 43.736 mA mM$^{-1}$ cm$^{-2}$ [52]. Karimian et al. demonstrated the Zr-MOF with TiO$_2$ functionalized graphene oxide@UiO-66 (TGO@UiO-66) for simultaneous detection of paraoxon and chlorpyrifos. The square wave voltammogram (SWV) of TGO@UiO-66/GCE in presence of paraoxon and chlorpyrifos showed two characteristic peaks at 0.45 and 1.3 V. The designed sensor exhibited low detection limits of 0.2 and $1.0 \times 10^{-9}$ M within the linear ranges of $1 - 100 \times 10^{-9}$ M and $5 - 300 \times 10^{-9}$ M for paraoxon and chlorpyrifos [53]. Bhardwaj et al. reported the three-phase composite material consisting of SiO$_2$-coated Cu-MOF, single layer graphene, and aniline was synthesized. In presence of ammonium persulfate as an oxidant, the aniline component of this mixture was polymerized to polyaniline to bridge Cu-MOF with graphene. The sensor showed wide linear range from 1 - 100 ppm with LOD of 1 ppm [54].

Lu et al. demonstrated the graphene aerogel (GA) with Zr-based MOF composites was developed for simultaneous detection of multiple heavy-metal ions in aqueous solutions. The sensor showed lower LODs for simultaneously detecting multiple metal ions were $9 \times 10^{-9}$ M for Cd$^{2+}$, $1 \times 10^{-9}$ M for Pb$^{2+}$, $8 \times 10^{-9}$ M for Cu$^{2+}$, and $0.9 \times 10^{-9}$ M for Hg$^{2+}$. Finally, the practical applications in detecting Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ in river water and the leaching solutions of soil and vegetable also demonstrated [55] Figure 7. Li et al. reported the Cu-based MOF using 1,3,5-benzenetricarboxylic acid (BTC) with high-conductivity ball-mill-exfoliated graphene (Cu-BTC@GS) by a simple method. The composite materials showed better electrocatalytic activity towards the biomolecules (xanthine and hypoxanthine) and phenolic pollutants (BSA and p-chlorophenol) by double potential step chronocoulometry [56]. Li et al. reported the Cu centered MOF with graphene composites (Cu-MOF-GN) [Cu-MOF = Cu$_3$(BTC)$_2$ (BTC = 1, 3, 5-
benzenetricarboxylic acid) and then modified on GCE (Cu-MOF-GN/GCE). The electrochemical sensor exhibited a wide linear concentration from $1.0 \times 10^{-6}$ to $1.0 \times 10^{-3}$ M with the detection limits of $5.9 \times 10^{-7}$ M for HQ and $3.3 \times 10^{-7}$ M for CT (S/N = 3) [57].

Baghayeri et al. demonstrated the novel nanocomposite of graphene oxide with zinc-based MOF (GO/Zn-MOF) was prepared by a simple solvothermal method. The electrochemical As(III) sensing capability of the nanocomposite was explored by casting the GO/Zn-MOF on GCE, followed by an electrochemically reduction of GO. The present sensor showed excellent electrochemical performance such as a wide linear range from 0.2 to 25 ppb (mg/L), LOD (S/N = 3) of 0.06 ppb and good reproducibility [58]. Peng et al. reported the porphyrinic Zr-MOF with reduced graphene oxide (PCN-224/rGO) nanocomposite for $p$-arsanilic acid ($p$-ASA). The PCN-224/rGO nanocomposite had strong affinity to $p$-ASA via Zr–O–As coordination and π–π stacking. The developed composite sensor had a wide detection range from 10 ng L$^{-1}$ to 10 mg L$^{-1}$, with a LOD 5.47 ng L$^{-1}$. Finally, the sensor was successfully applied to monitor $p$-ASA in simulated natural water and swine manure lixivium [59]. Gan et al. reported the highly
dispersed Au nanorods and GO-wrapped microporous ZIF-8 were successfully encapsulated inside the ZIF-8 (AuNRs@ZIF-8) by epitaxial growth or nucleus coalescence. The microporous ZIF-8 shell functions as a protective coating to effectively prevent AuNRs from dissolution, aggregation, and migration during the electrochemical testing of four pesticides as niclosamide, dichlorophen, carbendazim, and diuron [60] Figure 8.

Figure 8. Scheme showing the synthesis of AuNRs@ZIF-8@GO [60]. Reprinted with permission from [60] Copyright (2019) Royal Society Chemistry.

Ding et al. reported the newly developed chemically functionalized 3D graphene oxide hydrogels (FGH) decorated with MOFs-derived Co₃O₄ nanostructures and then utilized for sensing of acetone. The sensor showed good sensitivity with linear range concentration from 4.01/1 ppm to 81.2/50 ppm with response time ~ 20 s [61]. Travlou et al. reported the hybrid material consisting of Cu-based MOF with aminated graphite oxide for ammonia sensor. A hybrid material with the smallest content of graphene phase exhibited the largest signal change upon exposure to ammonia [62].

Chen et al. demonstrated the preparation of Cu-based MOF-199 with GO by solvothermal and then used for electrochemical determination of CT and HQ. It showed wide linear range from 0.1 to \(566 \times 10^{-6}\) M for CT and 0.1 to 476 μM for HQ with the same LOD of 0.1 μM (S/N = 3) [63]. Wang et al. reported the incorporation of rGO into a MIL-101(Cr) for the modification of CPE and then utilized for electrochemical sensors. The resulted electrodes exhibited high sensitivity and reliability in the simultaneous
identification and quantification of CC and HQ. It shows linear wide range concentration from 10 to $1400 \times 10^{-6}$ M and 4 to $1000 \times 10^{-6}$ M, and LODs were 4 and $0.66 \times 10^{-6}$ M (S/N=3) for CC and HQ [64]. Wang et al. demonstrated the new type of Cu-BTC on electro-reduced GO (ERGO) by electrodeposition. The modified electrode was used for highly sensitive determination of 2,4,6-trinitrophenol (TNP) by DPV. It shows three reduction peaks, the first at a potential of $-0.42$ V (vs. SCE) and wide linear range concentration from 0.2 to $10 \times 10^{-6}$ M TNP with LOD $0.1 \times 10^{-6}$ M (S/N=3) [65]. The performance of the MOF with graphene based composite fabricated electrochemical sensors was compared and the results are given in Table 2 [51-53,55,57-59,63-65].

Table 2. Comparison of performance of the various MOFs-graphene based electrochemical sensors towards the detection of toxic chemicals, environmental pollutants and isomeric phenolic compounds.

<table>
<thead>
<tr>
<th>Sensing material</th>
<th>Technique</th>
<th>Analytes</th>
<th>Linear range (M)</th>
<th>Detection limit (M)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-MOF/ERGO</td>
<td>DPV</td>
<td>BSA</td>
<td>$0.02 - 90 \times 10^{-6}$</td>
<td>$6.7 \times 10^{-9}$</td>
<td>51</td>
</tr>
<tr>
<td>Cu-MOF/rGO</td>
<td>AMP</td>
<td>Nitrite</td>
<td>$3 - 40000 \times 10^{-6}$</td>
<td>$33 \times 10^{-9}$</td>
<td>52</td>
</tr>
<tr>
<td>TGO@UiO-66</td>
<td>SWV</td>
<td>Paraoxon</td>
<td>$0 - 100 \times 10^{-9}$</td>
<td>$0.2 \times 10^{-9}$</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chlorpyritos</td>
<td>$5 - 300 \times 10^{-9}$</td>
<td>$0.1 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>GA-UiO-66-NH$_2$</td>
<td>DPV</td>
<td>Cd$^{2+}$</td>
<td>$0.01 - 1.5 \times 10^{-6}$</td>
<td>$9 \times 10^{-9}$</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb$^{2+}$</td>
<td>$0.001 - 2 \times 10^{-6}$</td>
<td>$1 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu$^{2+}$</td>
<td>$0.01 - 1.6 \times 10^{-6}$</td>
<td>$8 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hg$^{2+}$</td>
<td>$0.001 - 2.2 \times 10^{-6}$</td>
<td>$0.9 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>Cu-MOF-GN</td>
<td>DPV</td>
<td>HQ</td>
<td>$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$</td>
<td>$5.9 \times 10^{-7}$</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CT</td>
<td>$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$</td>
<td>$3.3 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>GO-Zn-MOF</td>
<td>DPV</td>
<td>As(III)</td>
<td>$0.2 - 25$ ppb</td>
<td>$0.06$ ppb</td>
<td>58</td>
</tr>
<tr>
<td>PCN-224/rGO</td>
<td>PEC</td>
<td>p-ASA</td>
<td>$10$ ng L$^{-1}$ – $10$ mg L$^{-1}$</td>
<td>$5.47$ ng L$^{-1}$</td>
<td>59</td>
</tr>
<tr>
<td>Cu-MOF-199 GO</td>
<td>DPV</td>
<td>CT</td>
<td>$0.1 - 566 \times 10^{-6}$</td>
<td>$0.1 \times 10^{-6}$</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HQ</td>
<td>$0.1 - 476 \times 10^{-6}$</td>
<td>$0.1 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>MIL-101 rGO</td>
<td>DPV</td>
<td>CC</td>
<td>$10 - 1400 \times 10^{-6}$</td>
<td>$4 \times 10^{-6}$</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HQ</td>
<td>$4 - 1000 \times 10^{-6}$</td>
<td>$0.66 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Cu-MOF/ERGO</td>
<td>DPV</td>
<td>TNP</td>
<td>$0.2 - 10 \times 10^{-6}$</td>
<td>$0.1 \times 10^{-6}$</td>
<td>65</td>
</tr>
</tbody>
</table>

* Bisphenol A (BSA); Hydroquinone (HQ); Catechol (CT); Photoelectrochemical (PEC); p-arsanilic acid (p-ASA); Trinitrophenol (TNP), Square-Wave Voltammetry (SWV); Differential pulse voltammetry (DPV).
Rani et al. reported the porous Zn-MOF@rGO, synthesized via solvothermal technique and then utilized for the amperometric determination of hydrazine. The Zn-MOF@rGO solution was used to modify on gold electrode (AuE) for the superior electrocatalytic oxidation of hydrazine in real water sample. TEM studies revealed prismatic shape of Zn-MOF with size ranging between 160 and 180 nm and were well-dispersed on the rGO sheets. The hydrazine sensor using Zn-MOF@rGO as electrocatalyst displayed a low LOD, high sensitivity and a fast response time (< 2s) [66]. Tung et al. reported the graphene hybrid nanocomposite with MOFs including copper, benzene-1,3,5-tricarboxylate (pG-Cu BTC), zirconium 1,4-dicarboxybenzene (pG-Uio 66) and 2-methylimidazole zinc salt (pG-ZIF 8), were investigated to enhance the sensing performance and capability of distinguishing different VOC biomarkers (e.g., methanol, ethanol, chloroform, acetone, acetonitrile and THF). It showed that the pG-Cu BTC sensor has the highest sensitivity and selectivity towards chloroform and methanol VOCs at 2.82 - 22.6 ppm level [67] Figure 10.

Figure 10. Schematic showing the concept of VOC biomarkers detection for human health monitoring by using graphene-based MOFs hybrid nanocomposites [67]. Copyrighted by Elsevier (2020).

Gu et al. reported the Cr-based MOF (MIL-101(Cr))/ rGO electrocatalyst was prepared through a one-pot hydrothermal method. The obtained results imply that, compared to the single components, it exhibits higher electrocatalytic activity for the reduction of metronidazole and stripping of Cd$^{2+}$ and Pb$^{2+}$. Optimizing the ratio of MIL-101(Cr) and rGO, an electrochemical sensor was prepared using MIL-101(Cr)/rGO-20 and used for detection of metronidazole, Cd$^{2+}$ and Pb$^{2+}$, respectively. The linear range for metronidazole can be divided into two parts, i.e. from 0.5 to 200 mM and from 200 to 900 mM and limit of detection is 0.24 mM (S/N=3, n=10). Another one is the wide linear
range from 0.05 to 6.0 mM for the detection of Cd\(^{2+}\) and Pb\(^{2+}\) with detection limits found to be 5.2 and 3.0 × 10\(^{-6}\) M (S/N=3, n= 10), respectively [68]. Yu et al. displayed the carboxyl-functionalized graphene, a highly sensitive electrochemical sensor for Pb\(^{2+}\) was proposed by using 8–17 DNA enzymes as the recognition element and the reaction of H\(_2\)O\(_2\) catalyzed by Fe-MIL-101 as the signal probe. It shows excellent sensing performance with a wide linear and LOD of 1.74 × 10\(^{-14}\) mol·L\(^{-1}\) and high selectivity to Pb\(^{2+}\) [69]. Tu et al. reported the rGO-encapsulated with Ce-MOF (rGO@Ce-MOF) composite was synthesized by using a simple and green method. Then, the obtained rGO@Ce-MOF composite was utilized as electrode material for the detection of dichlorophen (Dcp) and wide linear range from 0.02 to 10 × 10\(^{-6}\) M and a low detection limit of 0.007 × 10\(^{-6}\) M (S/N = 3) [70]. Kung et al. demonstrated the graphene nanoribbons (GNRs) are incorporated with the nanocrystals of a porphyrinic-MOF by solvothermally growing MOF-525 in a suspension of well-dispersed GNRs. The uniform thin films of MOF-525/GNR nanocomposite can be simply deposited on conducting glass substrates by drop casting and then applied for electrochemical nitrite sensors. The sensor showed wide linear range from 100 to 2500 × 10\(^{-3}\) M (R\(^2\) = 0.998), and sensitivity of the nitrite can be estimated to be 93.8 mA mM\(^{-1}\) cm\(^{-2}\) with LOD is calculated to be 0.75 × 10\(^{-3}\) M [71]. Xie et al. reported the graphene aerogels (GAs) and ZIF-8 nanocrystals were orderly grown on the surface of PPy/GAs through the coordination interaction between Zn\(_2\) and amino groups in PPy chains. This hybrid 3D architecture provided open channels for electrolyte transportation and improved electron transfer between the electrode and the catalysts, which was exploited as electrochemical sensing platform for the detection of highly toxic 2, 2methylenebis (4-chlorophenol) (dichlorophenol, Dcp) with LOD 0.1 × 10\(^{-9}\) M [72]. Zhang et al. reported the chromium terephthalate MOFs (MIL-101(Cr) with rGO was proposed to improve the electrical conductivity of MIL-101(Cr) crystals. The electrocatalytic applications of MIL-101(Cr)@rGO nanocomposites were employed for the voltammetric study of 4-nonylphenol and linear range concentration from 0.1 to 12.5 × 10\(^{-6}\) M with a LOD of 33 × 10\(^{-9}\) M [73]. Yang et al. reported the Cu\(_3\)(btc)\(_2\) MOF using BTC is covalently immobilized at chitosan (CS) with electrochemically reduced graphene oxide (ERGO) hybrid film modified electrode. The modified electrode utilized for electrocatalytic application of HQ, CT and RC and linear range from 5.0 to 400 × 10\(^{-6}\) M, 2.0 to 200 × 10\(^{-6}\) M and 1.0 to 200 × 10\(^{-9}\) M with LOD 0.44, 0.41 and 0.33 × 10\(^{-9}\) M for HQ, CT and RC [74] Figure 11. Yan et al. reported the bimetallic MOF-818@reduced graphene oxide/multi-walled carbon nanotubes (RGO/MWCNTs) composite was successfully synthesized by a facile solvothermal method. The MOF-818@RGO/MWCNTs/GCE exhibits an excellent
electrocatalytic activity towards phenolic acid compounds: caffeic acid (CA), chlorogenic acid (CGA) and gallic acid (GA). The sensor shows two linear ranges from 0.2 to $7 \times 10^{-6}$ M and 7 to $50 \times 10^{-6}$ M with a high sensitivity of 12.89 $\mu$A/$\mu$M for the detection of CA, a low detection limit of $5.7 \times 10^{-9}$ M and an excellent sensitivity of 12.50 $\mu$A/$\mu$M in the ranges of 0.1 to $3 \times 10^{-6}$ M and 3 to $20 \times 10^{-6}$ M for CGA detection, as well as a comparable electrochemical performance for GA [75]. Ling et al. reported the amine-functionalized MOF/reduced graphene oxide (NH$_2$-MIL-125/RGO) was prepared by a one-pot hydrothermal reaction. Then it was successfully hybridized with GO, and NH$_2$-MIL-125/RGO then modified on the GCE. NH$_2$-MIL-125/RGO/GCE displayed a high sensitivity and outstanding stability for the detection of BPA because of the synergistic effects of large surface area of GO and high porosity of NH$_2$-MIL-125. The sensor showed linear with the wide concentration of BPA from 2 to $200 \times 10^{-6}$ M, and LOD of $0.7966 \times 10^{-6}$ M [76].

Figure 11. Scheme showing the synthesis of hybrid based Cu$_3$(btc)$_2$/CS–ERGO/GCE for electrocatalytic application of HQ, CT and RS [74]. Reprinted with permission from ACS [74] (2016).
Table 3. Comparison of performance of the various MOFs-graphene based electrochemical sensors towards the detection of toxic chemicals, environmental pollutants and hydroxyl phenols.

<table>
<thead>
<tr>
<th>Sensing material</th>
<th>Technique</th>
<th>Analytes</th>
<th>Linear range (M)</th>
<th>Detection limit (M)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-MOF@rGO</td>
<td>AMP</td>
<td>Hydrazine</td>
<td>0.001 – 100 × 10^{-6}</td>
<td>8.7 × 10^{-3}</td>
<td>66</td>
</tr>
<tr>
<td>MIL-Cr/rGO</td>
<td>DPV</td>
<td>Cd^{2+}</td>
<td>0.5 – 200 × 10^{-3}</td>
<td>5.2 × 10^{-6}</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb^{2+}</td>
<td>0.05 – 6.0 × 10^{-3}</td>
<td>3.0 × 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>rGO@Ce-MOF</td>
<td>DPV</td>
<td>Dcp</td>
<td>0.02 – 10 × 10^{-6}</td>
<td>0.073 × 10^{-6}</td>
<td>70</td>
</tr>
<tr>
<td>GNIR-MOF-525</td>
<td>AMP</td>
<td>Nitrite</td>
<td>100 – 2500 × 10^{-3}</td>
<td>0.75 × 10^{-3}</td>
<td>71</td>
</tr>
<tr>
<td>MIL-101 (Cr)/rGO</td>
<td>DPV</td>
<td>4-nonylphenol</td>
<td>0.1 – 12.5 × 10^{-6}</td>
<td>33 × 10^{-9}</td>
<td>73</td>
</tr>
<tr>
<td>Cu_{3}(btc)_{2}/CS-ERGO</td>
<td>DPV</td>
<td>HQ</td>
<td>5 – 400 × 10^{-6}</td>
<td>0.44 × 10^{-6}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CT</td>
<td>2 – 200 × 10^{-6}</td>
<td>0.41 × 10^{-6}</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RS</td>
<td>1 – 200 × 10^{-9}</td>
<td>0.33 × 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>NH_{2}-MIL-125/rGO</td>
<td>DPV</td>
<td>BPA</td>
<td>2 – 200 × 10^{-6}</td>
<td>0.7966 × 10^{-6}</td>
<td>76</td>
</tr>
<tr>
<td>Ni-MOF-GO</td>
<td>DPV</td>
<td>p-CNB</td>
<td>0.1 – 300 × 10^{-6}</td>
<td>8.0 × 10^{-9}</td>
<td>77</td>
</tr>
<tr>
<td>AuNRs@ZIF-8</td>
<td>DPV</td>
<td>DCP</td>
<td>0.01 – 15 × 10^{-6}</td>
<td>3.0 × 10^{-9}</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CBZ</td>
<td>0.002 – 2.5 × 10^{-6}</td>
<td>0.33 × 10^{-9}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>DU</td>
<td>0.001 – 20 × 10^{-6}</td>
<td>0.26 × 10^{-9}</td>
<td></td>
</tr>
<tr>
<td>3D Co-MOF/rGO</td>
<td>DPV</td>
<td>RS</td>
<td>0.1 – 800 × 10^{-6}</td>
<td>1.9 × 10^{-8}</td>
<td>79</td>
</tr>
</tbody>
</table>

Bisphenol A (BPA); Hydroquinone (HQ); Catechol (CT); Resorcinol (RS); Dichlorophen (Dcp); p-chloronitrobenzene (p-CNB); Carbendazim (CBZ).

Gao et al., reported the sensitive determination of toxic organic pollutant p-chloronitrobenzene (p-CNB) using Ni based MOF (Ni-MOF) and GO. The composite sensor showed superior electrocatalytic performance towards the oxidation of p-CNB in a concentration range of 0.1 to 300 × 10^{-6} M, and LOD 8.0 × 10^{-9} M (S/N = 3) [77]. Gan et al. reported the AuNRs@ZIF-8 with encapsulated in GO nanosheets to enhance the
chemical resistance of the multicore–shell support. The composite material was modified on electrode surface and then sensor showed wide linear range from $0.01$ to $15 \times 10^{-6}$ M for DCP, from $0.002$ to $2.5 \times 10^{-6}$ M for CBZ, and from $0.001$ to $20 \times 10^{-6}$ M for DU with LOD are $3.0$, $0.33$, and $0.26 \times 10^{-9}$ M for DCP, CBZ, and DU, respectively [78]. Topcu et al. demonstrated the 3D Co-MOF with rGO (Co-MOF/rGO) composite paper was prepared with a facile electrochemical deposition of Co-MOF on the surface of rGO paper electrode. And then utilized for electrocatalytic application of RS with a large linear range from $0.1–800 \times 10^{-6}$ M and a LOD $1.9 \times 10^{-8}$ M [79]. The performance of the MOF with graphene based composite fabricated electrochemical sensors was compared and the results are given in Table 3 [66,68,70,71,73,74,76-79].

4. Challenges and opportunity

The above research on the MOF with graphene-based nanocomposite fabricated electrochemical sensors results showed that MOFs are becoming a very effective tool for electrochemical sensing applications [80-82]. Generally, MOF materials are less conductance and their electrical conductivity and redox activity must be improved to enhance their performance. The MOFs with a variety of graphene oxide composites for facilitate an excellent conductivity to the composite material. Finally, most of the MOFs with graphene-based nanocomposites were highly exploited towards the determination of biologically important compounds. However, their utility in the detection of toxic metal ion, environmental pollutants, nitro compounds and hazards vapor with solvents are still not elaborated in the research. Hence, their application in the electrochemical sensing of nitro compound, environmentally pollutant, toxic anion and toxic chemicals is very limited in the literature. Thus, the utilization of the MOFs with graphene based nanostructures in the electrochemical sensing of the aforementioned compounds will make a new platform with excellent sensitivity in the near future.

Conclusions

In this chapter, we discussed the various MOFs with graphene-based nanocomposites for electrochemical sensing of toxic chemicals, environmental pollutants, nitro compounds, heavy metal ions, hazards solvents and vapors. The MOFs with graphene oxide, reduced graphene oxide and other graphene-based nanocomposites have been synthesized by various synthetic approaches like solvothermal, reflux, stirring, microwave and sonochemical. Initially, electrochemical sensing application of heavy metal, toxic compounds, nitro compounds and environmentally hazards using MOF modified electrodes. Then MOFs with graphene oxide based nanocomposites utilized to enhance the electrocatalytic sensing application through synergetic effect of both components. It
has been detected in many studies that the MOFs with graphene based nanocomposites can enhance the electrocatalytic activities for different species like metal ions, anions, pesticides, environmental pollutants, nitro compounds and important biologically important compounds. In recent years has been witnessed significant interest in the development of MOFs with graphene-based nanocomposite for electrochemical sensors. The electrodes modified with different functionalized MOFs with graphene-based nanocomposites introduced in this review were generally seen to have improved sensitivities than the ones modified with MOF, graphene oxide, reduced graphene oxide and bare electrodes. This may be due to the fact that the nanocomposite modified electrodes had increased electrochemical surface coverage of the MOFs and graphene based modified electrodes. Many of the MOFs with different graphene-based nanocomposites discussed in this analysis showed good sensitive and selective towards the analytes due to the synergetic effect, π–π interactions of analytes with compound and active surface area. Finally, MOFs with graphene based nanocomposites were highly exploited towards the determination of toxic chemicals, environmental pollutants, nitro compounds and carcinogenic compounds.

References


