Recent advances on electrochemical methods in fabricating two-dimensional organic-ligand-containing frameworks

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Abstract
Organic-ligand-containing frameworks have drawn considerable attention due to their multifunctional properties as well as tunable structures for broad applications. Among numerous synthesis methods developed in the past two decades, electrochemical processing has been demonstrated as one of the most efficient, safe, and facile ways to realize the large-scale and highly controllable production of organic-ligand-containing frameworks. In this review, the progress of electrochemically induced crystallization and thin film fabrication of organic-ligand-containing frameworks is summarized in a well-rounded way. Besides, the mechanism and processing parameters are also discussed. Moreover, the main challenges are also expounded for providing some guidance on the future development of organic-ligand-containing frameworks, especially for covalent-organic frameworks and hydrogen-bonded organic frameworks.

Keywords
covalent organic frameworks, electrophoretic deposition, electrosynthesis, films, hydrogen-bonded organic frameworks

Abbreviations: 2-MeIm, 2-methylimidazole; AA, acetic acid; BDC, terephthalic acid; BTC, 1,3,5-benzenetricarboxylic acid; BTPA, benzene-1,3,5-triyltriboronic acid; COFs, covalent organic frameworks; CTAB, cetyltrimethylammonium bromide; DABDC, 2,5-diaminoterephthalate; DCM, dichloromethane; DMF, N,N-dimethylformamide; DMI, 1,3-dimethyl-2-imidazolidinone; DMSO, dimethyl sulfoxide; ECD, electrochemical deposition; EPD, electrophoretic deposition; Et₃NH⁺, triethylammonium; EtOH, ethanol; FTO, fluorine-doped tin oxide; GC, glassy carbon; GCE, glassy carbon electrode; H₃BTB, benzene-1,3,5-tris(4-benzoic acid); H₄BTEC, 1,2,4,5-benzenetetracarboxylic acid; HER, hydrogen evolution reaction; HHTP, 2,3,6,7,10,11-hexahydroxytriphenylene; HOFs, hydrogen-bonded organic frameworks; HOPG, highly oriented pyrolytic graphite; IBED, indirect bipolar electrodeposition; ITO, indium tin oxide; Ln-MOFs, lanthanide-based MOFs; MeOH, methanol; MILs, Matériaux Institut Lavoisier metal-organic frameworks; MOFs, metal-organic frameworks; MTBS, tributylmethylammonium methyl sulfate; MTCP, meso-tetra(4-carboxyphenyl)porphine; OER, oxygen evolution reaction; PMMA, polymethyl methacrylate; pTAPP, polymeric film of TAPP; Py, 4,4′,4″-(pyrene-1,3,6,8-tetrayl)tetraaniline; SCE, saturated calomel electrode; TAPP, 5,10,15,20-tetraakis(4-aminophenyl)porphyrin; TBA PF₆, tetrabutylammonium hexafluorophosphate; TEA PF₆, tetrathylammonium hexafluorophosphate; TPTC, 2,4,6-trihydroxy-1,3,5-benzenetricarboxaldehyde; Vg²⁺, 2Cl⁻, 1,1-Bis(4-formylphenyl)−4,4′-bipyridinium dichloride; ZIFs, zeolitic imidazolate frameworks.

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1 | INTRODUCTION

Organic-ligands-containing frameworks including metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and hydrogen-bonded organic frameworks (HOFs) have attracted a lot of attention due to their tunable pore size and predesigned structures, which offer them wide applications in a variety of fields, such as gas adsorption and separation, catalysis, optoelectronics, electrochromic, energy, sensing, and drug delivery.\(^1\)\(^{-12}\)

Although hundreds of novel organic-ligand-containing frameworks as well as their applications have been explored in the past decades, there is still a daunting task to realize their industrialization due to the lack of an efficient approach to obtain high-quality and well-patterned organic-ligand-containing frameworks.\(^{13,16,17}\)

For instance, the large-scale preparation of precisely controlled thin films based on organic-ligand-containing frameworks has attracted considerable interest.

So far, numerous approaches have been developed for the fabrication of thin films based on organic-ligand-containing frameworks, including seed growth,\(^ {17}\) Langmuir–Blodgett layer-by-layer deposition,\(^ {18}\) gel-layer synthesis,\(^ {19}\) interfacial strategy,\(^ {14}\) solution epitaxy,\(^ {20,22}\) spin-coating\(^ {23,24}\) dip-coating,\(^ {25,26}\) and chemical vapor deposition.\(^ {27}\)

However, all the above-mentioned approaches are often multistep, high-cost, time-consuming, and low-controllability.

To address these issues, a novel electrochemical technology comes to the view of scientists as this method has been proven to be environmental-friendly, time-saving, easy-performing, and precise-controllability.\(^ {13,28-30}\)

Electrochemical deposition (ECD) and electrophoretic deposition (EPD) are two widely used methods of electrochemical technology for the preparation of thin films based on organic-ligand-containing frameworks.\(^ {16,30-32}\)

EPD consists of two main processes, namely electrophoresis (promoting the charged particles migrate toward the substrates with the opposite charge under appropriate electric field) and electrodeposition (depositing the charged particles onto the surface of the substrates by interfacial bonding, electric field force, and electrostatic force). Similar to EPD, ECD also contains electrophoresis and electrodeposition processes. Besides, it has a third process, namely, electrochemical reactions (including electrochemical redox, protonation/deprotonation) before the electrophoresis and electrodeposition.\(^ {16}\)

In this review, we focus on the widely used electro-synthesis methods (i.e., ECD and EPD) in the preparation of organic-ligand-containing frameworks (i.e., MOFs, COFs, and HOFs) as well as the fabrication of their thin films (Figure 1). The proposed mechanisms (such as anodic dissolution, cathodic deposition, direct EPD, etc.) are summarized, followed by the advances of corresponding researches. Moreover, the relationship and differences of electro-synthesis among MOFs, COFs, and HOFs are discussed. We hope that this review would provide some guidelines for the future synthesis and the large-scale industrial application of organic-ligand-containing frameworks.

2 | MOFS

To date, hundreds of types of MOFs are synthesized through diffusion,\(^ {33,34}\) hydrothermal/solvothermal/surfactant-thermal approach,\(^ {35}\) microwave,\(^ {36}\) mechan-chemical method,\(^ {37}\) and sonochemistry.\(^ {38}\)

Normally, these approaches cannot directly offer film modes or coatings, which limits the application of as-synthesized MOFs. Fortunately, MOFs are one class of compounds constructed by inorganic metal ions or clusters coordinated to organic ligands. In other words, over the course of the synthesis, metals are in their oxidation state, meaning that metal species are charged. This property offers the targeted MOF an opportunity to be prepared via low-cost, rapid, and environmental-friendly electro-synthesis.\(^ {13,16,26}\)

The metal ion source required for the construction of MOFs can be directly provided from its own metal substrate (like plate, coil, foil, etc.) by the applied electric field due to the electrochemical oxidation. Besides, the resulted metal ions will further react with organic ligands to form MOFs and deposit on the surface of the electrode. Here, two well-rounded mechanisms of ECD and the principle of EPD in the electro-synthesis of MOFs are summarized.

![Schematic applications of electrosynthesis in fabrication of organic-ligand-containing frameworks](image-url)
2.1 Anodic ECD

The most well-known electrosynthesis method is anodic dissolution proposed by Mueller et al. in 2005. After published, this method has drawn huge attention due to its mild synthetic condition, precise controllability, time saving, and the possibility of industry-scale production. Besides, the metal ions required for the construction of MOFs are offered by the electrode oxidation instead of metal salt sources in the solution, which avoids the variation in the kinetics of MOF formation. The mechanism of anodic dissolution has been systematically investigated by Fransaer et al. Briefly, four parts (nucleation, growth of islands, intergrowth, and detachment) happen in this approach (Figure 2), which is further confirmed by Dryfe et al. via the in-situ electrochemical atomic force microscopy:

(i) Nucleation: the anodic metal electrode releases metal ions required for the formation of MOFs near the electrode surface (often in the double layer). Then, metal ions react with organic ligands to form nanocrystals. These nanocrystals nucleating on the electrode surface tend to start from the defects of the substrates.

(ii) Growth of MOF islands: after the nucleation existing on the substrate, the new nanocrystals are inclined to progressively nucleate at adjacent sites, thereby forming large crystals unless the critical nucleation threshold is surpassed.

(iii) Intergrowth: it is the most important part. The nanocrystals are continuously nucleating on the electrode surface. Meanwhile, at the already nucleated sites, the MOFs are gradually growing into large ones with dimensions of several microns, and finally cover the whole conductive substrate to form a compact layer.

(iv) Detachment: due to the uninterrupted release of metal ions from the anodic electrode, a lot of voids are formed between the MOF layer and the electrode surface, leading to the buckling of the MOF layer and finally resulting in the detachment. Besides, the formation of charged intermediates may also cause the occurrence of detachment due to the electrostatic repulsion (vide infra).

2.1.1 M-BTC

Cu-BTC (also termed as HKUST-1, BTC = 1,3,5-benzenetricarboxylic acid) is the first MOF synthesized via anodic ECD introduced by Mueller et al., where two Cu plates were employed as both cathode and anode and methanol (MeOH) as a solvent to dissolve BTC. The octahedral Cu-MOF was afforded by anodic ECD conducted under the condition of constant current for 2.5 h. Inspired by this research, E. De Vos et al. briefly investigated the parameters that affected the formation of Cu-BTC and found that the crystal sizes could be tuned over a wide range from 2 to 50 μm by the simple alternation of the applied voltage, the reaction time, and the addition of water. Notably, adding appropriate water to the reaction mixture could slow down the crystal formation and yields larger crystals. Also, based on the principle of anodic ECD, that is, the formation of the MOFs is strictly limited to the Cu-covered areas under an appropriate condition, the authors innovatively incorporated MOFs onto a predesigned Cu pattern, which opens the eyesight for the fabrication of functional microelectronic devices. To further understand the effects of parameters including solvents, temperature, and current density on the growth of Cu-BTC, Gascon et al. employed the controlled variates to investigate them in detail. According to their report, Cu-BTC could be obtained by soaking two Cu electrodes with a distance of 3 cm into an ethanolic aqueous solution containing 0.15 mol/L BTC as ligands and

FIGURE 2 Proposed mechanism of MOF anodic electrodeposition and SEM pictures, taken at a 75° angle with the normal, of the four phases: (I) initial nucleation (A), (II) growth of islands (B), (III) intergrowth (C) (III) and detachment (D). Below are the corresponding SEM images. Copper-coated wafer substrate, 2 V versus counter electrode, after 10 s, 10 min, 60 min, and 125 min. Reproduced with permission under CC BY 3.0 (https://creativecommons.org/licenses/by/3.0/); Copyright 2016, Royal Society of Chemistry.
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0.33 mol/L tributylmethylammonium methyl sulfate (MTBS) as supporting electrolyte under the conditions of various constant current modes. Almost uniform Cu-BTC could be found when the ratio of ethanol (EtOH) was above 75 vol%, otherwise another coordination polymer, catenatriaquama-(1,3,5-benzenetricarboxylate)-Cu(II), would be formed. 3.5 times and 7 times increases in conductivity by adding more supporting electrolytes could only raise the yield by a factor of 1.6 and 2, respectively, while the reaction temperature (no more than 80°C) does not show any significant influence on the yield. However, the morphology of pure Cu-BTC would change with the reaction temperature. For instance, octahedral crystals were obtained at 20°C whereas cubic crystals were harvested at 200°C. Intriguingly, the square wave functions led to better results in terms of electrodes coverage than that of continuous current because of the fact that the inhibiting effect of concentration polarization is mitigated.

Inspired by the research on Cu-BTC, Cao et al. first introduced ECD to prepare fluorescent Zn-BTC thin films on the anodic Zn plate, where a bath solution was prepared by dissolving 10 mol/L of H3BTC as ligands and 10 mol/L of ammonium fluoride as supporting electrolyte into deionized water and subsequently purged oxygen out by N2 at 65°C for 1 h. Under the optimized conditions (2 V for 40 s), the rod-shaped MOF microcrystals featuring zigzag chains of Zn2+ ions connected by alternate BTC3+ linkers grew on the anodic Zn plate, and further extended into a three-dimensional network via hydrogen bonds, thereby forming the uniform and compact MOF films (Figure 3A,B). Similarly, the average roughness and thickness of as-prepared MOF films are time- and voltage-dependent, that is, the MOF films feature epitaxial growth with increasing time. Furthermore, the defects of as-prepared MOF films are reduced with increasing applied voltage, which can be ascribed to the fact that the aggregation of Zn2+ cations and BTC3- anions near the anode surface induced by the increase of applied voltage offers more nucleation sites and nutrients, thereby favoring the formation of MOF films. Recently, the anodic dissolution approach has also been extended to co-deposition. For instance, Ghaffarinejad et al., for the first time, tunably synthesized two different MOFs (i.e., Cu-BTC and Zn-BTC) simultaneously via the anodic dissolution approach. The synthesis was conducted in 10 ml of EtOH/H2O (with different ratios) containing 0.15 mol/L of BTC as ligands and 0.33 mol/L of MTBS as supporting electrolyte. A three-electrode system with potentiostatic mode was employed, in which the brass alloy (65% Cu and 35% Zn) served as both working electrode and counter electrode, and the Ag/AgCl (3 mol/L KCl) acted as the reference electrode. A series of influencing parameters including the solvent effect, the synthesis time, and the applied potential were carefully investigated. From the scanning electron microscope (SEM) images, the increasing ratio of water could decrease the deprotonation of the BTC and enhance the hydration of metal ions, thereby slowing down the crystal formation and yielding large crystals. The high ratio of water would lead to the formation of fibrous morphology. Notably, the desirable MOFs could be selectively formed by rational control over the applied potential due to the different reduction potentials of Zn and Cu. In addition, the increase of voltage could accelerate the MOF nucleation process but decrease the size of the MOF particles due to the formation of more Cu and Zn cations. By the way, Fe-BTC was also reported to be electrosynthesized by Achmann et al., however, the authors did not show any structural characterizations in detail.

Besides common metals such as Cu and Zn, lanthanides also come to the view of scientists due to their unique physical and chemical properties and special atomic orbitals. Fransaer et al. employed an anodic process for the first time to fabricate lanthanide-based MOFs (Ln-MOFs) with good crystallinity and fibrous-needle morphology, namely Gd-BTC, Tb-BTC, and Gd-BTC doped with Tb(Gd(Tb)-BTC), via anodic ECD approach. An EtOH/demineralized water (1:1 vol/vol) mixture containing 32.10 mmol/L of MTBS as a supporting electrolyte and 47.59 mmol/L of H3BTC as ligands was prepared. The ECD was conducted at 60°C for 15 min under a constant current of 1 mA/cm², in which Ga foil (for Gd-BTC and Gd(Tb)-BTC) and Tb foil (for Tb-BTC) were used as working electrodes and a Pt foil (ca. 5 cm²) was selected as a counter electrode. Strikingly, these

![Figure 3](image)
Ln-MOFs could be deposited on Tb(III)-doped ZnO substrate under the same condition as that for Tb-BTC. Cao et al.\textsuperscript{50} also reported a cathodic electrochemically-assisted microwave approach for the fabrication of Ln-MOFs (vide infra). However, the above-mentioned two methods are only applicable for lanthanide-modified substrates.\textsuperscript{49,50} Due to the high cost of lanthanide, both methods are impractical in industrial production. Given that, Cao et al.\textsuperscript{51} further directly employed the EPD method to deposit Tb-BTC, Eu-BTC, and Eu\textsubscript{0.45}Tb\textsubscript{0.55}-BTC films on unmodified substrates (e.g., Zn plate, indium tin oxide [ITO] glass, and fluorine-doped tin oxide [FTO]) in their own suspension under 90 V DC voltage in 5 min, respectively. The EPD process can be directly conducted thanks to the carboxylate groups that give rise to some negative surface charge of the as-formed MOFs.

2.1.2 | Zeolitic imidazolate frameworks (ZIFs)

ZIFs are a subfamily of MOFs, which self-assemble to form metal-imidazolate-metal structure with zeolite-like topologies.\textsuperscript{52,53} Compared with other MOFs, ZIFs are stable (even in boiling alkaline solution) and can be synthesized under mild conditions.\textsuperscript{52,54,55} However, the preparation of ZIF thin films is often complicated and requires high temperature.\textsuperscript{54,56–59} Referring to the application of anodic ECD in the fabrication of Cu-BTC, Gascon et al.\textsuperscript{44} for the first time, synthesized ZIF-8 via anodic ECD.\textsuperscript{44} Two Zn electrodes with a distance of 3 cm were soaked into a solution (i.e., N,N-dimethylformamide [DMF], MeOH, EtOH, or H\textsubscript{2}O) containing 0.15 mol/L of 2-methylimidazole (2-MeIm) and 0.1 mol/L of appropriate electrolyte (i.e., MTBS, Na\textsubscript{2}SO\textsubscript{4}, KNO\textsubscript{3}, or KCl) under constant current modes. The advantage of anodic ECD of ZIF-8 is wide temperature window (even at 0°C) and the yield increases linearly with the applied current density. It worth noting that the formation of ZIF-8 requires an incubation time (ca. 10 min) before the nucleation due to the crystallization kinetics, which is quite different from anodic ECD processes of almost all MOFs.\textsuperscript{44,54,60} In addition, based on the property of electric field-induced electrochemical reaction, Kuhn et al.\textsuperscript{61} innovatively proposed the indirect bipolar electrodeposition (IBED) to wirelessly and selectively deposit MOF monomers onto metallic substrates for the preparation of Janus-type composite without using masks or templates (Figure 4A).\textsuperscript{61}

![Figure 4](https://example.com/fig4.png)

**Figure 4** (A) Mechanism of the formation of ZIF-8. Crystal growth on the anodically polarized side of a Zn wire is triggered by IBED (top) and design of the bipolar electrochemical cell used for the synthesis of ZIF-8 (bottom). (B) Control experiment without electric field after 3 days in a solution containing 2-MeIm (1.376 mol/L) and Na\textsubscript{2}SO\textsubscript{4} (0.05 mol/L) (top); Synthesized by the IBED method (6 V, 60 min, 1.376 mol/L 2-MeIm, 0.05 mol/L Na\textsubscript{2}SO\textsubscript{4}) (middle); SEM images of as-synthesized ZIF-8 by IBED (6 V 60 min, 1.376 mol/L 2-MeIm, 0.05 mol/L Na\textsubscript{2}SO\textsubscript{4}) (bottom). (C) Copper bead (3 mm diameter) obtained at 10 V, in the presence of H\textsubscript{2}BTC (0.08 mol/L) in EtOH after 60 min reaction time (top); Corresponding SEM images of Cu-BTC as-synthesized by IBED on the copper bead (bottom). Reproduced with permission: Copyright 2014, John Wiley and Sons.\textsuperscript{61} IBED, indirect bipolar electrodeposition; ZIF, zeolitic imidazolate framework
The IBED approach makes use of the electrochemically induced local change in pH around the conducting object, which realizes the goal of controlled polymerization or precipitation of an insulating deposit and further improves the generality of the ECD approach. For instance, identical ZIF-8 with rhombic decahedral morphology and uniform size of ca. 4 μm could be formed on the partial side of Zn wire under the optimal condition (6 V for 60 min) (Figure 4B). The IBED approach can be applied to the synthesis of Cu-BTC as well (Figure 4C).

### 2.1.3 | MILs

Matériaux Institut Lavoisier metal-organic frameworks (MILs) formed by the combination of trivalent metals and the corresponding organic ligands are another subfamily of MOFs, which was first reported by Férey et al. Similarly, the traditional synthesis (i.e., hydrothermal method) is rigorous and multisteped, and requires high temperature, which limits the application of MILs. Given that, Gascon et al. employed anodic ECD to prepare MILs (i.e., MIL-100(Al), MIL-53(Al), and NH2-MIL-53(Al)). For the preparation of MIL-100(Al), similar to the rigorous hydrothermal conditions, it can only be fabricated by soaking two Al electrodes separated by 3 cm into a mixture of EtOH/H2O (75:25 vol/vol) containing 0.119 mol/L of BTC under the condition of 10 mA/cm2 above 60°C for 1 h. Moreover, MIL-53(Al) and NH2-MIL-53(Al) with the feature of breathing effect were electrochemically synthesized in H2O/DMF mixtures containing 0.1 mol/L KCl as supporting electrolyte and 0.091 mol/L of terephthalic acid (BDC) for MIL-53(Al) or 0.082 mol/L of 2-aminoterephthalic acid for NH2-MIL-53(Al) with two Al electrodes spaced 3 cm apart at 90°C. Interestingly, the as-obtained MIL-53(Al) exhibits large pore (lp) configurations instead of narrow pore (np) configurations in hydrothermally synthesized samples. Furthermore, in NH2-MIL-53(Al), the pore configurations can be tuned from the lp configuration to the np configuration by increasing the voltage ratio of DMF. The temperature limitations over the course of ECD or EPD cannot be bypassed due to the boiling point of solvent until Fransaer et al. proposed a novel high-temperature and high-pressure electrochemical cell for the first time to synthesize MIL-100(Fe), which is inaccessible by ECD at low temperature. Two kinds of solutions, solution A (an EtOH/H2O 2:1 vol/vol mixture containing 47.59 mmol/L H2BTC) and solution B (the absolute EtOH containing 95.17 mmol/L H2BTC with 64.21 mmol/L of MTBS as the supporting electrolyte), were prepared for fabricating MOF layers and producing larger amounts of MOF in suspension, respectively. The pure Fe plate and Cu plate were selected as the anode and cathode, respectively. As a result, MIL-100(Fe) could be formed at a wide range of temperature from 110 to 190°C and current densities ranging from 2 to 20 mA/cm2. Intriguingly, the solution composition led to various types of formation, that is, adding MTBS increased the current density but favored the production of MOF in solution rather than on the surface of the electrode, and vice versa. Moreover, higher temperatures are favorable for monodisperse small crystals probably since the nucleation is temperature-activation compared to the ensuing crystal growth, leading to the formation of uniformly sized coating nanocrystals.

### 2.1.4 | Others

In contrast to the above-mentioned bivalent metals (i.e., Cu (II) and Zn(II)) and trivalent metals (i.e., Al(III), Fe(III), Gd (III), Tb(III), Eu(III), Yb(III), Er(III)), the high-valent Zr(IV)-based Zr6O4(OH)8(BDC)6 framework, termed UiO-66, has been firstly synthesized through ECD (Figure 5A). The Zr foils acted as both anode and cathode and were soaked in a synthesis solution containing BDC:NH2:2H2O:glacial acetic acid (AA):DMF = 1:2:4:5/10:50:130 (the corresponding AA concentration is 0.5, 1, and 5 mol/L, respectively). Subsequently, the ECD process was conducted under 20 mA/cm2 of constant current at 383 K for 30 min. With increasing the concentration of AA modulator from 0.5 to 1 mol/L, more compact and smoother UiO-66 films could be fabricated, however, the crystallite sizes continuously decreased (Figure 5B, C).

Liu and Chen et al. proposed a novel electrochemical synthesis method for the fabrication of large-area Cu(II)/HHTP2 MOF film on the single-crystal Cu(100) anode. The electroosynthesis solution was prepared by dissolving 8.107 mg of 2,3,6,7,10,11-Hexahydroxiphenylene (HHTP) powders into 100 ml of deionized water/EtOH (1:1 vol/vol) mixture. Notably, 30 μl of ammonia was dropped to promote the dissolution and ionization of HHTP. Then, the pretreated anodic Cu(100) foil was passed through the solution at a rate of 0.5 cm/min and 3 cm apart from the counter electrode (Figure 6A). Under an appropriate applied voltage, a homogenous Cu(II)/HHTP2 MOF thin film featuring A-A stacking and excellent crystallinity (the average size of the crystalline domain is nearly 80 nm) was obtained. Notably, over the course of anodic ECD, the electrolysis rate of anodic Cu could be regulated from 2 × 10−1 mol/(cm2·s) to 12 × 10−1 mol/(cm2·s) by directly adjusting the applied voltage, which offered the facile control over the morphology and thickness of as-prepared MOF films. However, with increasing the applied voltage, more as-synthesized MOFs were found in the solution instead of on the Cu(100) foil. A convincing elucidation of this phenomenon is that a small amount of released Cu2+ ions under the low voltage tend to
form negatively charged $[\text{Cu}_3\text{(HHTP)}_2]^{3-}$ flakes in the presence of HHTP anions and adhere onto the anodic Cu surface due to the electrostatic attraction (Figure 6B). In contrast, a large amount of Cu$^{2+}$ released by high voltage would combine HHTP anion and incline to form $[\text{Cu}_3\text{(HHTP)}_2]^{2+}$ flakes, resulting in detachment because of the electrostatic repletion (Figure 6C). The upper limit of the film thickness is ca. 60 nm. More importantly, the as-synthesized MOF thin films can be easily transferred into arbitrary substrates without any damage by polymethyl methacrylate transfer technology. This strategy is also useful for the preparation of Cu$_5$(MTCP), Cu$_5$(BTPA)$_2$, and Cu$_3$(TBTC)$_2$ MOF films.

Recently, the amine-based manganese MOF, namely Mn-DABDC(ES), was synthesized by Iqbal and Easun et al. via electrochemical method under the optimal conditions of 70 mA current for 2 h at room temperature, and the yields were as high as 93%. A distilled water/DMF (1:3 vol/vol) solution containing 75 mmol/L of 2,5-diaminoterephthalic acid and 67.5 mmol/L of NaNO$_3$ was prepared. Two cleaned Mn strips were immersed into the bath solutions with a distance of 2 cm before the electrosynthesis. According to the XRD pattern, the Mn-DABDC(ES) features a good crystallinity.

The anodic ECD is available for the fabrication of various MOFs. The extremely high selectivity of MOFs can be achieved by adjusting the applied potential because the reductive potentials of metal ions provided by anodes are different. Therefore, the anodic-dissolution-synthesized MOFs often feature good crystallinity as well as good properties. For instance, the electrosynthesized Mn-DABDC(ES) exhibits higher CO$_2$ and H$_2$ adsorption than that of solvothermally synthesized Mn-DABDC(ST). Moreover, the anodic ECD endows UiO-66 good crystallinity as well as unique aggregation mode, thereby providing it with an excellent capability of sampling and concentration of volatile organics. Occasionally, the electrochemically synthesized MOFs may endow contrast properties. For example, the MIL-53(Al) and NH$_2$-MIL-53(Al) synthesized via the electrochemical method do not show any breathing over the course of CO$_2$ adsorption, which is contrary to the hydrothermally synthesized ones.
2.2 | Cathodic ECD

Compared with anodic dissolution, cathodic electro-synthesis is quite new, which was first proposed and well investigated by Dincă et al.\textsuperscript{28,70–72} Normally, in the cathodic ECD process, the so-called probase (i.e., nitrate) can trap electrons supplied by cathodic substrates and undergo reductive reaction to produce OH\textsuperscript{−} (Equation 1), which increases the pH near the cathode surface, thereby promoting the deprotonation of neutral bridging ligands required for the synthesis of corresponding MOFs (Figure 7A).\textsuperscript{31,67} Due to the electric field force, the metal cations will migrate towards the cathode and coordinate with the deprotonated ligands to form MOFs. Compared with anodic dissolution in which the anodic substrates must be the same with respect to the MOFs, the cathode mainly serves as an electron reservoir instead of involving in the reaction of MOF electrosynthesis, that is, cathodic ECD does not have substrate limitation and almost all conductive substrates (e.g., ITO, FTO, metals, glassy carbon [GC], etc.) can serve as the electrode.\textsuperscript{13,28,70,73} Intriguingly, at least for MOF-5, the second layer grows at the bottom of the first one if two layers are sequentially fabricated, which is opposite to the anodic dissolution ECD (Figure 7B). Thus, the undercut-induced detachment in anodic dissolution (vide supra) can be circumvented in cathodic ECD.\textsuperscript{40} However, the cathodic ECD needs demanding conditions, otherwise the metal plating will take place simultaneously, which results in the impurity of the as-synthesized MOFs.\textsuperscript{70,74,75}

\begin{equation}
\text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad (1)
\end{equation}

2.2.1 | Traditional cathodic ECD

Constructing MOFs through the electrochemically induced reductive reaction was first proposed by Dincă et al.,\textsuperscript{28} where the crystalline Zn₄O(BDC)₃ (MOF-5) was successfully synthesized on the cathode (Figure 8A). The in-situ deprotonation of neutral ligands plays a crucial role in fabricating anionic-ligand crystalline materials. Accordingly, the cathodic generation of OH\textsuperscript{−} is in favor...
of the deprotonation of neutral bridging ligands to form the anionic ligands tending to coordinate with metal cations, thereby forming MOFs on the cathode surface. Given that, they prepared the reaction mixture by dissolving Zn(NO$_3$)$_2$ and H$_2$BDC in DMF/H$_2$O (100:1 vol/vol) solution in which the 0.1 mol/L tetra-butylammonium hexafluorophosphate (TBA PF$_6$) serves as the supporting electrolyte. Then, the deposition process was conducted on the FTO substrate at a constant potential of $-1.6$ V versus Ag/Ag(cryptand)$^+$ for 15 min, during which the current density almost generally increased from $-5.4$ to $-6.6$ mA/cm$^2$. Finally, the rough films with thickness varying from 20 to 40 μm were obtained. Nevertheless, the purity of as-synthesized MOF-5 phase is terrible because the high reduction overpotential causes the Zn plating on the cathode surface simultaneously. To circumvent this problem, the authors chose triethylammonium (Et$_3$NH$^+$) with a relatively higher reduction potential to replace nitrate, because one of the products (H$_2$) was a relatively inert and insoluble molecule that would not interfere with MOF formation (Equations 2–4).$^{70}$ Meanwhile, the inert electrode (Pt) was selected as the working electrode due to its excellent catalysis for proton reduction. In the electrolyte containing Zn(NO$_3$)$_2$, H$_2$BDC, and Et$_3$NH$^+$ (≥300 mmol/L), a white crystalline film, (Et$_3$NH)$_2$Zn$_3$(BDC)$_4$, was obtained without any Zn plating at a constant potential of $-1.00$ V (Figure 8C). Notably, when the applied reductive potential further increased to $-1.5$ V, there was not any observation of Zn plating. Nevertheless, when the concentration of Et$_3$NH$^+$ decreased to 100 mmol/L, a mixed film composed of MOF-5, Zn, and (Et$_3$NH)$_2$Zn$_3$(BDC)$_4$, could be observed at a constant potential of $-1.5$ V (Figure 8D and 8E). When the applied reductive potential increased to $-1.7$ V, the electrodeposition mainly gave the film composting of Zn and MOF-5. These phenomena probably come from that the high concentration of Et$_3$NH$^+$ acid could etch the plated Zn as well as prevent the accumulation of Et$_3$N. When the concentration of Et$_3$NH$^+$ decreased to a certain level, it would not interfere with the formation of (Et$_3$NH)$_2$Zn$_3$(BDC)$_4$ featuring lower absolute value of reductive potential but waken the buttering capacity, thereby leading to the accumulation of Et$_3$N and the increase in pH, which perhaps results in the formation of a second crystalline MOF phase with the feature of a higher absolute value of reductive potential. Based on these, the fabrication of mixed films can be achieved and so do the sandwich-type bilayer structures (Figure 8B). Furthermore, the role of water in the electrosynthesis of MOF-5 was disclosed.$^{71}$ The proportion of MOF-5 increased with the H$_2$O content during the electro-reductive reaction, however, H$_2$O is not an initial necessity at the occurrence of the deposition of MOF-5 because the nitrate reduction on the cathode will generate water in the presence of H$_2$BDC (Equations 1 and 4). Moreover, nitrate anions play essential roles in the formation of the layered hydroxide phases, especially with Zn$_4$(OH)$_4$(H$_2$O)-(NO$_3$)$_2$ as intermediates, and the formation of Zn$_4$O(O$_2$C$_2$)$_6$ secondary building units, thereby accelerating the formation
of MOF-5 (Figure 8F). Notably, in the absence of nitrate, the water and oxygen can also serve as the $\mu_4$-O$^{2-}$ in the Zn$_4$(O$_2$C$^-$)$_6$ secondary building units, leading to the formation of MOF-5 under cathode bias.$^{72}$

$$2\text{R}_3\text{NH}^+ (\text{R} = \text{alkyl}) + 2e^- \rightarrow \text{H}_2 + 2\text{R}_3\text{N} \quad (2)$$

$$2\text{H}_2\text{BDC} + 2e^- \rightarrow \text{H}_2 + 2\text{HBDC}^- \quad (3)$$

$$\text{NO}_3^- + \text{H}_2\text{BDC} + 2e^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + \text{BDC}^{2-} \quad (4)$$

Besides Zn-based MOFs, the cathodic ECD is also applicable for the construction of Cu-based MOFs. Yang et al. successfully electrosynthesized three copper MOFs (Cu-MOFs) on the cathode via the direct reduction approach.$^{73}$ Three types of ligands, 1,2,4,5-benzenetricarboxylic acid (H$_4$BTEC), H$_2$BDC, and H$_3$BTC, were employed to form Cu-MOFs, termed Cu-BTEC, Cu-BDC, and Cu-BTC, respectively. In the course of synthesis, the glassy carbon electrode (GCE) was utilized as the cathode and the $-1.3$ V of constant voltage was applied for 5 min. In addition, the 0.01 mol/L
of Et₃NHCl was added to adjust the pH value, thereby regulating the deprotonation rates to slow down the formation of coordination bonds between the organic ligands and copper centers, meaning that the nucleation rate of MOFs was reduced, facilitating the formation of large-sized particles. These as-obtained Cu-MOFs exhibit good stability in electrochemical measurements and in water at room temperature for at least 10 min and 4 h, respectively. To further understand the regulation and the effect of applied cathodic potential on the synthesis of MOFs, the authors further prepared Cu-BTC via cathodic ECD under the same condition except the cathodic potential ranging from −1.1 to −1.4 V (step −0.1 V, vs. saturated calomel electrode [SCE]). As a result, the thickness of these as-synthesized Cu-BTC films increased with the absolute value of applied potential, however, the sizes of nanosheets were opposite. This can be attributed to the acceleration of the reduction of H₂O:AA:DMF = 1:2:4:10/50:130 (the concentrations of the corresponding AA are 1, and 5 mol/L, respectively) under 20 mA/cm² of constant current at 383 K for 30 min (Figure 5D,E). In the cathodic deposition, the AA acts as carrier species, enabling the anode-released Zr(IV) transporting through the solution to the surface of the cathode. Interestingly, the increase of AA concentration would lead to the tendency of cathodic deposition (vide supra) due to the increased competition for complexation of released Zr(IV) (Figure 5A). Notably, the cathodic deposition of UiO-66 can be successfully performed on a broad of conductive substrates including metallic zirconium, metallic titanium, and titanium nitride on top of a silicon wafer.

2.2.2 Structure-directing cathodic ECD

Surfactants are a class of organic compounds featuring unique amphiphilicity which have been widely used as structure-directing agent for the synthesis of predesigned organic-ligand-containing frameworks. Additionally, inspired by the electrochemically assisted self-assembly technique, Nematollahi et al. proposed a strategy for fabricating a zinc-containing mesoporous metal-organic framework (Zn-mMOF) thin films on both sides of the cathodic electrode surface without the need for any ex-situ base/probase or contemplate. They employed a standard three-electrode setup with a platinum counter electrode and a GC working electrode in an undivided cell containing H₃BTC as a ligand, zinc nitrate as a cation source, and cetyltrimethylammonium bromide (CTAB) surfactant as a structure-directing agent, to successfully synthesize the Zn-mMOF thin films under controlled-potential conditions (E_app = −1.3 V vs. SCE) or galvanostatic conditions (I_app = 3 mA/cm²) for 10,800 s (Figure 10A). In this procedure, the critical process is the in-situ electrogeneration of hydroxide ions (contributed by the water and NO₃⁻) at the cathode surface, which increases the local pH in the electrode double layer, leading to the deprotonation of the ligands, thereby causing the crystallization of the mMOF on the cathode surface. Notably, the electrostatic attraction between the anionic ligands (L⁻) and cationic surfactant (S⁺) results in the crystallization process and the growth of the mMOF (Figure 10B). Therefore, the addition of the surfactant can not only contribute to the perpendicularly aligned 3D hollow hexagonal morphology but also results in the 2D hierarchical honeycomb-like mesoporous structure without any damage to the original MOF structure (Figure 10C–H), and the well-defined crystallinity was proven by the wide-angle PXRD pattern. According to the ICP data, the amount of zinc ion is as high as 22.99 wt% (the theoretical value is 23.99 wt%). Besides,
Silvester et al. improved the methodology for cathodically depositing microporous particles of Cu-BTC on a GCE by employing a potential-step chronoamperometric approach at room temperature. The plating bath was prepared by evenly mixing the 10 ml of aqueous phase (containing 0.45 mol/L of copper nitrate trihydrate and 10 mol/L of sodium nitrate) and 10 ml of organic phase (containing 0.25 mol/L of H$_3$BTC as an organic ligand and 0.27 mol/L of CTAB surfactant as a structure-directing agent) together, and subsequently adding 50% HCl to adjust the pH to 2.0 ± 0.2. Then, the electrodeposition was conducted under −1.4 V (vs. external Ag/AgCl(aq) reference electrode) for 2 h, in which a GC stub acted as a working electrode and a Pt coil acted as a counter electrode. The cathodic deposition occurred near the surface of the electrode, so the increase of pH only occurred at the interface instead of the bulk solution, which favored the deprotonation of the BTC ligands. Also, the structure-directing agent CATB provides the enhanced wettability and directs the negatively charged BTC ligands towards the electrode surface to take place the coordination reaction with Cu$^{2+}$, thereby fabricating the Cu-BTC with a well-defined shape of cuboctahedron (chamfered cubic) structure. Remarkably, the efficient hydrogen evolution prevents metal deposition on the surface of the working electrodes.

### 2.2.3 Oxygen-assisted cathodic ECD

To circumvent the metal plating problem over the course of the cathodic ECD, Lu et al. proposed an oxygen-assisted cathodic deposition strategy to synthesize a series of ZIFs (ZIF-8, ZIF-71, and ZIF-67) with the advantages of highly tunable thickness and the non-plating of metallic deposition (Figure 11A). An air-saturated precursor solution was prepared by dissolving chloride salts (ZnCl$_2$ or CoCl$_2$) and imidazole ligands in MeOH, and subsequently were purged.
with air for 30 min, in which the O$_2$ concentration was about 2 mmol/L. In the presence of supporting electrolyte TBA PF$_6$, ZIF-8 was successfully prepared on the freshly-peeled highly oriented pyrolytic graphite (HOPG) cathode under the condition of $-0.7$ V (vs. Ag/AgCl [3 mol/L KCl]) for 2 h at room temperature. The domain sizes of the intergrown crystals increased from 100 to 600 nm with prolonging reaction time from 2 to 12 h. Intriguingly, further decreasing the applied voltage, for instance from $-0.9$ to $-1.0$ V, would promote the nucleation of ZIF-8 on the surface of HOPG but decrease the domain sizes of the crystals. It is worth noting that no metallic plating can be found during the process due to the more positively reductive potential of O$_2$ to O$_2^-$. ZIF-71 and ZIF-67 can also be synthesized by bridging 4,5-dichloroimidazole (dclM) with Zn(II) and HmIM with Co (II), respectively. In addition, two kinds of copper-carboxylate MOFs (Cu-BTC and MOF-14 [Cu$_3$BTC$_2$, H$_3$BTC = benzene-1,3,5-tris(4-benzoic acid)]) were also prepared without any metallic plating through the oxygen-assisted cathodic deposition (Figure 11B).$^{75}$ The synergistic catalytic effects of the acidic copper ions and BTC ligands on the O$_2$ reduction can positively shift the deposition potential of Cu-BTC significantly to +0.05 V (vs. Ag/AgCl 3 mol/L KCl), which is far positive than that of the plating of metallic copper. For the deposition of Cu-BTC, a dimethyl sulfoxide (DMSO) solution containing 10 mmol/L of Cu(NO$_3$)$_2$ and 5 mmol/L of H$_3$BTC was prepared due to the strong interactions between the DMSO molecules and Cu$^{2+}$ as well as the formation of hydrogen-bonded between DMSO and H$_3$BTC, which endows this precursor solution with good stability. The influential parameters including the temperature, the presence/absence of supporting electrolyte, the concentration of O$_2$, and the applied voltage were systematically investigated. The higher temperature (120°C), the absence of supporting electrolyte, lower O$_2$ concentration, and more positively applied voltage (0.05 V) will favor the formation of larger crystal domains but slow down the nucleation of MOFs, and vice versa (Figure 11C–E). Also, the prolongation of reaction time can back up the larger crystal size.

2.2.4 | Others

Cao et al.$^{50}$ reported an electrochemical-assisted microwave approach to fabricate Ln-MOFs on FTO glasses (Figure 12A). Briefly, microwave irradiation can convert the lanthanide hydroxide layers onto the FTO (Ln(OH)$_3$/FTO) substrate.
prepared through the electrodeposition of Ln-MOFs (Figure 12B–E). This method is available for several Ln-MOFs including Tb-MOF, Eu-MOF, Yb-MOF, and Er-MOF.

Bloch and coworkers extended the synthetic strategy of MOFs containing coordinatively unsaturated, redox-active metal cations by introducing the electrochemical method. During the electrochemical process, the oxidation state of dissolved metal cations can be tuned through the controlled potential electrolysis. Based on this method, a highly-qualified Ti(III)-MIL-101 film was achieved by electrochemical reduction under cathodic bias of −1.2 V (vs. Ag/AgNO₃) for 4 h in a cathodic cell containing a solution of 16.5 ml of anhydrous DMF:EtOH (10:1) in the presence of 0.03 mol/L of TiCl₄, 0.024 mol/L of H₂BDC, and 0.1 mol/L of TBA PF₆ as the supporting electrolyte, followed by heating at 120°C for 18 h. The proton balance and high selectivity can be achieved by the proposed electrochemically synthetic strategy of reduced metal frameworks, which in part contributes to the formation of the identical structure of Ti(III)-MIL-101. In contrast to the increase of H⁺ released by the deprotonation of ligands, the proposed electrosynthetic approach provides a means to manage H⁺, thereby control over
the pH value during the synthesis. Also, the potential of hydrogen evolution reaction (HER) activity on the nickel-foam-based working electrodes is far lower than that of the reduction potential of Ti$^{4+}$. As a result, this electrochemical strategy has been successfully extended to fabricate a series of reduced metal-organic frameworks including Ti(III)-MIL-100, Ti(III)-MIL-101-bpdc, and Ti(III)-MIL-100-tatb under the similar condition.

Cathodic ECD is different from the anodic ECD. Although it does not have substrate limitation, which may benefit for the preparation of the MOFs with noble metals or rare earth elements, the purity of the as-synthesized MOFs is often poorer than the expectation due to the occurrence of metal plating. This problem can be ascribed to the reductive potential because the synthesis is often negative compared with the metal ion. Therefore, it is necessary to explore a sacrificial agent (e.g., the above-mentioned O$_2$) with appropriate reductive potential to further improve the purity of as-synthesized MOFs. Notably, taking the advantage of cathodic ECD, the MOFs can grow on conductive substrates with different shapes or spatial structures to achieve excellent performance. For instance, ZIF-67 can be uniformly fabricated on the surface of Ni foam with three-dimensional spatial structure and subsequently be transformed into porous carbon materials (CNT networks) for HER and oxygen evolution reaction.

### 2.3 Direct EPD

Farha and Hupp et al. introduced EPD into the fabrication of nominally neutral MOF films (e.g., NU-1000, UiO-66, Cu-BTC, and MIL-53(Al)) and co-deposited MOF films (Figure 13). These four kinds of MOFs exhibited net negative surface charge charge probably due to some surface defects, for example, missing linkers or metal nodes. For the EPD process, a MOF suspension was prepared by adding 10 mg of MOF powder into 20 ml of toluene solution and sonicated for 30 s to make sure homogeneous dispersion; then two FTO glasses were immersed into the suspension, followed by 90 V of DC voltage for 3 h. Strikingly, in conjunction with photolithography, a predesigned micropatterned MOF thin film is accessible by EPD (Figure 13B, below). Furthermore, two types of MOF films can be directly deposited onto a single conductive substrate via EPD.

Apart from the EPD towards the anode, Zhang et al. also employed the EPD method to deposit ZIF-67 particles onto the cathodic FTO glass to form thin films. A suspension was obtained by ball milling 100 mg ZIF-67 powder together with 4 ml isopropanol for 4 h and being subsequently diluted 10 times by isopropanol and sonicating for 15 min. The EPD process was conducted under constant electric fields ranging from 20 to 60 V/cm for fixed 1 min, and the corresponding thickness ranges from...
1.0 to 7.0 μm. Thanks to the surface defects resulted from the ball milling, more Co ions can be exposed to provide ZIF-67 particles with positive surface charge, which smoothly promotes the EPD process. Notably, the crystallinity does not show any damage during the EPD, which is demonstrated by the PXRD pattern. Additionally, the deposited ZIF-67 thin film can undergo vulcanization to form porous Co9S8 thin films, which exhibits better catalytic activity to oxidize vanillin.

EPD is one of the most facile methods for the controllable preparation of MOF thin films without obvious damage to the crystallinity as well as for the realization of uniformly micropatterned MOF thin films. Remarkably, different types of MOF films can be directly co-deposited onto the substrate, which backs up the construction of more complex and multifunctional surface architectures comprising of multiple MOFs.

3 | COFS

In contrast to the coordination bonds in MOFs, COFs are formed through the condensation/coupling reactions between organic precursors, resulting in the formation of strong covalent bonds to afford well-organized, stable, and crystalline organic frameworks. Since the first study published by Côté and Yaghi, tens of different linkages (e.g., boroxine, boronic ester, imine, hydrazone, azine, imide, C=C, 1,4-dioxin, etc.) have been developed for the fabrication of MOFs. Due to the lack of charged moieties, COFs are usually synthesized via solvothermal method, microwave approach, ionothermal synthesis, mechanochenical route, and interfacial strategy. Until recent years, the electrosynthesis of COFs experienced a rapid development. Nonionic COFs (e.g., COF-5, COF-300, and BDT-ETTA COF) and the ionic COF (e.g., PyVg-COF) can be directly coated or deposited on conductive substrates to form the corresponding thin films through EPD within a few minutes. Notably, the availability of ECD is demonstrated in the construction of porphyrin-based COFs.

3.1 | EPD

3.1.1 | Nonionic COFs

The EPD conditions are always harsh such as extremely high applied voltage since the almost electronuetral properties of nonionic COFs. For instance, Medina et al. have directly utilized EPD for the straightforward
preparation of COF thin films and coatings. The versatility of the proposed method was demonstrated by the successful fabrication of well-characterized COFs with two- and three-dimensional structures, which were linked by boronate-ester bonds or imine linkages (i.e., COF-5, COF-300, and BDT-ETTA COF) (Figure 14). All the COF monomers were synthesized under solvothermal conditions, and then simply suspended in an organic electrolyte with the features of nonconductivity and low dielectric constant (i.e., ethyl acetate, toluene, or anisole), followed by an appropriate sonication process to form homogeneous suspensions. Notably, ultrasound-based attrition of 20 kHz was employed to break down the intergrown agglomerates of BDT-ETTA COF into smaller particles before the suspension. The average particle sizes of approximate 200 nm were determined by dynamic light scattering measurements. For the EPD, the COF particles migrated to the anode under the electric field of 900 V/cm, indicating that the COF particles bearing an intrinsic negative surface charge without any modification, which was determined by Zeta-potential measurements. Interestingly, the intrinsic surface charge of the COF particles could be reversed by protonation. By the above-mentioned EPD, the COF films could be fabricated within 2 min on smooth or corrugated substrates and reach up to as large as 25 cm². The quantitative relationship between the thickness of COFs and EPD parameters was comprehensively investigated. For instance, the thickness of COF films linearly depended on the deposition time at a rate of 16 nm/s. Remarkably, the above-mentioned EPD was also applicable for the codeposition of COFs and COF/Pt nanoparticles from mixed suspensions. In the experiment of photoelectrochemical catalysis, the EPD BDT-ETTA COF films exhibit 19-times photocurrent density compared to that of dense and oriented thin BDT-ETTA COF films prepared by other methods, which can be ascribed to the enlarged interface between the photoabsorber produced by EPD. The COF/Pt hybrid film prepared by codeposition of Pt nanoparticles with BDT-ETTA COF further enhances the performance.

**FIGURE 14** (A) COF building blocks and their resulting frameworks used in the EPD. (B–D) SEM cross-section of (B) BDT-ETTA COF film, (C) COF-300 film, and (D) COF-5 film. The corresponding top-views are present at bottom with photographs of the film as in insets. Reproduced with permission: Copyright 2019, American Chemical Society. 94 COF, covalent-organic framework; SEM, scanning electron microscope
3.1.2 Ionic COFs

Compared to nonionic COFs, the deposition process of ionic COFs is quite mild due to their good solubility and charged moieties. Ma et al. synthesized an ionic COF, termed PyVg-COF, with the feature of high solubility via introducing high-density electrostatic repulsion to overcome the interlayer π-π stacking. The authors selected two building blocks with the contrasting properties, where 4,4′,4″-(pyrene-1,3,6,8-tetrayl)tetraaniline (Py) as one knot exhibited strong π-π interactions while 1,1-bis(4-formylphenyl)-4,4′-bipyridinium dichloride (Vg2+-2Cl−) as one linker showed strong electrostatic repulsion (Figure 15A). The PyVg-COF showed an extraordinary solubility and stability in organic solvents including N-methyl pyrrolidone, DMSO, DMF, N,N-diethylformamide, N,N-dimethylacetamide, and 1,3-dimethyl-2-imidazolidinone (DMI), which further facilitated EPD to form a thin film on ITO, gold, or stainless steel substrates. The principle of COF EPD film growth was shown in Figure 15B. Unlike unstable suspensions, the high solubility and stability of PyVg-COF provided the as-prepared thin film with excellent retention of solubility, porosity, crystallinity, and reproducibility. Notably, the thickness of PyVg-COF thin film could be well-controlled by regulating parameters of the applied electric field and the deposition time. The relationship between the thickness of the film and the parameters including the electric field intensity and deposition time has been quantitatively investigated. The thickness of the film was linearly increased with the electric field intensity with the rate at 1.4 nm/(V·cm) during the uniformly EPD deposition time of 20 s (Figure 15C). Under constant electric field intensity, the thickness of the film also linearly increased with the deposition time at the rate of 1.1 nm/s (Figure 15D). Remarkably, a 70 nm-thick film could be prepared within 20 s at an extremely low electric field intensity of

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**FIGURE 15** (A) Schematic representation of the synthesis of the PyVg-COF. (B) Scheme illustrating the principle of COF EPD film growth showing the attraction of the positively charged COF nanosheets toward the negatively charged electrode using an applied electric field. (C) Dependence of film thickness on the electric field intensity at an EPD time of 20 s. (D) Dependence of film thickness on the EPD time at an electric field intensity of 33.3 V/cm. Reproduced with permission under CC BY-NC 3.0 (https://creativecommons.org/licenses/by-nc/3.0/). Copyright 2019. A highly soluble, crystalline covalent organic framework compatible with device implementation. COF, covalent-organic framework.
Furthermore, because the film was only deposited on the electrodes, the morphology of the film could be regulated through tailoring the shape of employed electrodes. Intriguingly, unlike the pressed pellets, the as-obtained PyVg-COF film displays anisotropic electric property, that is, this COF film shows excellent conductivity in the interlayer orientation, while the intra-layer carrier conduction is inhibited. Similar to MOFs, the EPD can also be used in the deposition of monotype COFs as well as codeposition without obvious damage to the crystallinity. Due to the electroneutral properties of COFs, the aggregation is relatively loose, thereby enlarging the interface and improving the performance. Furthermore, the oriented deposition of ionic-COFs can be provided by the EPD.

3.2 | ECD

Distinguished from the EPD, the ECD is often accompanied with chemical reactions including redox reactions. Unlike MOFs, there are no metal centers in COFs that can undergo the redox reaction. Besides, the mechanism of electrosynthesis in organic chemistry is still not very clear, especially in macromolecules. Therefore, it is very difficult for scientists to employ ECD in the preparation of COFs. However, Siamak et al. innovatively proposed a strategy to synthesize
the poly(5,10,15,20-tetrakis(4-aminophenyl)porphyrin)-covalent organic frameworks, namely Py-POR-COF, via in-situ electrorystallization of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TAPP) (Figure 16A). A three-electrode system was employed to perform the electropolymerization in dichloromethane solution, in which the 0.25 mmol/L TAPP, 5% vol/vol pyridine, and 0.05 mol/L tetraethylammonium hexafluorophosphate (TEA PF6) served as the solute, the neutralizing agent, and the supporting electrolyte, respectively. Various conductive substrates (GC, ITO glass, and gold) were chosen as working electrodes, meanwhile, an Ag/AgNO3 and Pt gauze were used as the reference and counter electrodes, respectively. Notably, the potentiodynamic deposition during which the cyclic voltage varies from −0.4 V to 0.7 V, the galvanostatic deposition under 0.05 mA for 6 min, and the potentiostatic method under 0.6 V for 7 min are all applicable for the preparation of the free-standing polymeric film of TAPP (pTAPP). The mechanism showed that the radical cations of TAPP were formed, and then the oxidized para-aminophenyl substituents underwent coupling reactions, followed by the conversion from diphenylamines to dihydrophenazines and phenazine linkages. Notably, the potentialdynamic deposition during which the cyclic voltage varies from −0.4 V to 0.7 V, the galvanostatic deposition under 0.05 mA for 6 min, and the potentiostatic method under 0.6 V for 7 min are all applicable for the preparation of the free-standing polymeric film of TAPP (pTAPP). The mechanism showed that the radical cations of TAPP were formed, and then the oxidized para-aminophenyl substituents underwent coupling reactions, followed by the conversion from diphenylamines to dihydrophenazines and phenazine linkages. Notably, the pyridine is not only a neutralizing agent to reduce the acidic protons during the electropolymerization, but also can increase the interlayer spacing between adjacent 2D sheets through intercalating into the pTAPP networks, thereby stabilizing the structure and achieving the high crystallinity of Py-POR-COFs (Figure 16B,C). In addition, the parameters (i.e., temperatures, scan rates) on which the size of dendritic structure depends were investigated. The authors assumed that the growth of dendrites started from the pTAPP nanowire networks on the substrate, and then the nucleation occurred. Finally, the pTAPP crystals grew along the (110) planes because of the spherical diffusion on the nuclei and protrusions (Figure 16D). Remarkably, the crystalline dendrite Py-POR-COF thin film could be transferred into an organic electrolyte without any damage via the capillary force-assisted clean-stamp method.

The ECD is an efficient approach to synthesize the COFs with good crystallinity, but the mechanism has not been systematically established. Although the Py-POR-COF has been synthesized via ECD and its mechanism has been elucidated, the proposed strategy unlikely expands to other types of COFs, due to the specific structure of porphyrin. Besides, the mechanism proposed in MOFs is not well suitable for the synthesis of COFs due to the lack of metallic centers. However, electrons are one kind of catalysts involving in many organic reactions. Perhaps we can proceed from this point to design ECD for the fabrication of COFs.

4 | HOFS

Apart from the coordination bonding and covalent bonding, another organic framework termed HOFS can be constructed through intermolecular hydrogen bonding and other interactions. Benefiting from hydrogen bonding, most HOFS are solvent-processable. In addition, the presence of hydrogen donors and acceptors endows HOFS with the capability of incorporating other functional groups for diverse demands. For the film fabrication, the protonation/deprotonation will take place at sites of hydrogen donors and acceptors to form charged species, which creates the suitable conditions for EPD. Cao et al. first introduced the EPD into the fabrication of HOF-TCBP films and Eu@HOF-TCBP films on a series of conductive substrates including Zinc plates, Mg alloy plates, and FTO glass. The as-prepared HOF-TCBP or Eu@HOF-TCBP was
| Class Name | Medium | Electrolyte | Solvent | Electrosynthesis type | Condition | Substrate | Distance between electrodes | Reference |
|------------|--------|-------------|---------|----------------------|-----------|-----------|---------------------------|-----------|
| Cu-BTC     | Solution | MTBS | MeOH, EtOH, DMSO | Anodic ECD | 2 V for 20 min | Cu | 3 cm | 13,40 |
| Gd-BTCTb-BTCGd(Tb)-BTC | Solution | MTBS | EtOH/H₂O 7:3 | Anodic co-ECD | 10 V for 20 min | Brass alloy | 1 cm | 47 |
| ZIF-8      | Solution | MTBS | DMF, MeOH, EtOH, or H₂O | Anodic ECD | 1-30 mA cm⁻² (or square wave) for 33-1000 s | Zn | 3 cm | 44 |
| MIL-100(Al) | — | — | EtOH/H₂O 3:1 | Anodic ECD | 10 mA cm⁻² for 1 h at 60°C | Al | 3 cm | 44 |
| MIL-53(Al) | — | KCl, MTBS, NaOH | DMF/H₂O 1:9 | Anodic ECD | 2 mA cm⁻² for 3 h at 90°C | Al | 3 cm | 44 |
| NH₂-MIL-53(Al) | — | KCl, MTBS | DMF/H₂O 1:9 | Anodic ECD | 2 mA cm⁻² for 3 h at 90°C | Al | 3 cm | 44 |
| MIL-100(Fe) | Solution | EtOH/H₂O 2:1 | — | Anodic ECD | 2-20 mA cm⁻² for tens of seconds at 110-190°C | Fe | — | 45 |
| UiO-66     | Solution | — | DMF | Anodic ECD | 80 mA for 30 min at 100°C | Zr foil | 1.5 cm | 68 |

(Continues)
| Class Name | Medium | Electrolyte | Solvent | Electrosynthesis type | Condition Voltage and time | Current and time | Substrate | Distance between electrodes | Reference |
|------------|--------|-------------|---------|-----------------------|---------------------------|----------------------|-----------|--------------------------|-----------|
| Mn-DABDC(ES) | Solution | NaNO₃ | DMF/H₂O | Anodic ECD | 70 mA for 2 h | −6.6 mA cm⁻² for 15 min | Mn | 2 cm | 69 |
| MOF-5 | Solution | Zn(NO₃)₂ | DMF/H₂O 100:1 | Cathodic ECD | | | | | |
| Cu-BTECCu-BDC | Solution | Et₃HCl | DMF | Cathodic ECD | −1.3 V for 5 min | | | | 73 |
| ZIF-67 | Solution | Co(NO₃)₂·6·H₂O | MeOH/H₂O 19:1 | Cathodic ECD | −5.0 V vs Ag/AgCl for tens of seconds | | | | 77 |
| ZIF-71 | Solution | ZnCl₂ | — | Cathodic ECD | −0.8-0 V, 100 mV s⁻¹ for 2 h | | | | 74 |
| Ti(III)-MIL-101 | Solution | TBA PF₆ | DMF/EtOH 10:1 | Cathodic ECD | −1.2 V vs Ag/AgNO₃ for 4 h | | | | 83 |
| Class      | Name | Medium | Electrolyte  | Solvent     | Electrosynthesis type | Voltage and time | Current and time | Substrate         | Distance between electrodes | Reference |
|------------|------|--------|--------------|-------------|-----------------------|------------------|------------------|-------------------|----------------------------|-----------|
| Ti(III)-MIL-100 | Solution | TBA PF₆ | DMF/EtOH | Cathodic ECD | −1.2 V vs Ag/AgNO₃ for 4 h | Ni foam | — | 83 |
| NU-1000 | Suspension | — | Toluene | EPD | 90 V for 3 h | FTO | 1 cm | 84 |
| Tb-BTCEu-BTCP₃ | Suspension | — | DCM | EPD | 90 V for 5 min | ZnO, ITO, FTO | — | 51 |
| COF | COF-5COF-300BDT-ETTA COF | Suspension | — | EA/toluene/anisole | EPD | 900 V for 2 min | FTO | 1 cm | 94 |
| PyVg-COF | Solution | — | DMI | EPD | 10 V | ITO, Au, Stainless steel | — | 29 |
| pTAPP | Solution | TEA PF₆ | DCM | ECD | −0.4–0.7 V vs Ag/AgNO₃ for 10 cycles, 0.6 V for 7 min, 0.05 mA for 6 min | GC, ITO, Au | — | 95 |
| HOF | HOF-TCBP | Suspension | — | DCM | EPD | 90 V for 5 min | Zn, Mg, and FTO | 1 cm | 30 |
| Eu@HOF-TCBP | Suspension | — | DCM | EPD | 90 V for 5 min | Zn | 1 cm | 30 |
| PFC-1 | Suspension | — | DCM | EPD | 90 V for 2 min | FTO, Zn | 1 cm | 32 |
| PFC-13 | Suspension | — | DCM | EPD | 90 V for 5 min | Zn | 1 cm | 32 |

Abbreviations: DCM, dichloromethane; MOF, metal-organic framework; ZIF, zeolitic imidazolate framework.
dispersed in 20 ml of CH₂Cl₂ solution, followed by ultrasonication for 5 min, and then, the as-washed conductive substrates were immersed into the dispersion with 90 V of DC potential for 5 min. Finally, the dense and crack-free HOF films with high crystallinity were obtained. According to the SEM, the thickness was about 58 and 40 μm for the Eu@HOF-TCBP film and HOF-TCBP films, respectively. Besides, the as-obtained Eu@HOF-TCBP film shows reliable temperature sensing performance compared with the corresponding powders. Significantly, the generality of the proposed EPD strategy has been further demonstrated by the successful construction of the large scale or patterned PFC-1 and PFC-13 with the good capability of recycling (Figure 17).32

In summary, the accessibility of EPD is also demonstrated by the successful preparation of a series of HOF thin films. However, it is not persuasive to claim that the ECD can be successfully employed in the synthesis of HOFs because no such case has been reported so far (Table 1).

5 | CONCLUSION

Since the pioneering work regarding the electrosynthesis of organic-ligand-based frameworks, recent great progress has proven that electrosynthesis is one of the most efficient and highly controllable strategies to realize the industrial production of organic-ligand-based frameworks in the future. In this review, the development of widely-used electrosynthesis methods (i.e., ECE and EPD) are comprehensively summarized, as well as their mechanisms. For MOFs, ECD is well accessible due to the fact that metals and ligands can undergo oxidation or deprotonation, respectively. There are four steps in anodic dissolution (i.e., nucleation, growth of MOF island, intergrowth, and detachment). The anodic dissolution bears some merits including metal salt-free, selectivity, and pure phase owing to the metal ions supplied by the anodic-oxidation of metal substrates. However, the undercut-induced detachment limits the thickness of the MOF films. The principle of metal-ion release inhibits the large-scale production of MOFs with noble metals. In contrast, the cathodic ECD can well circumvent these drawbacks due to its distinct principle—deprotonation, in which the cathodic substrates only serve as electron reservoir instead of involving in the MOFs construction. However, the problem of metal plating hampers the development of cathodic ECD for a long time until the oxygen-assisted cathodic ECD has been proposed. In contrast, COFs are constructed via self-condensation to form covalent bonds between the organic ligands. Therefore, the traditional mechanism of ECD in MOFs cannot be directly introduced into the fabrication of COFs. Fortunately, the availability of ECD in COFs fabrication has been demonstrated by the successful synthesis of porphyrin-based COFs, namely Py-POR-COF. Nevertheless, it is still very difficult to claim that ECD is successfully accessible in the synthesis of HOF. Apart from the ECD, EPD can be directly employed in the fabrication of organic-ligand-containing framework thin films due to the surface charge on these three kinds of macromolecules.

Although ECD and EPD bear various merits of efficiency, simple apparatus, and large scalability, there still remain significant challenges for further developments. In spite of well-rounded ECD mechanisms in the MOF fabrication, there is not any systematic mechanism for the synthesis of COFs and HOFs. Additionally, compared with the numerous types of organic frameworks, only a few cases synthesized by ECD are reported, especially only one for COFs and none for HOFs, indicating that the application of ECD in the organic-ligand-based framework fabrication is in the early stage. The EPD has been demonstrated as an efficient way to prepare the corresponding thin films of MOFs and HOFs, but for almost electroneutral COFs, it requires harsh applied voltages as high as 900 V/cm.

Overall, using electrochemical methods to synthesize organic-ligand-containing frameworks and their corresponding thin films is an emerging research field. Especially, the advantages of electrosynthesis including efficiency, low cost, nonpollution, high quality, and precise selectivity make it become one of the most promising strategies to break the limitations of large-scale/area synthesis to meet up with industrialization in the future.

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CONFLICT OF INTERESTS

The authors declare no conflict of interest.

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