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Electrocatalytic conversion of CO_2 into selective carbonaceous fuels using metal-organic frameworks: An overview of recent progress and perspectives

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ABSTRACT

The tremendous increase in anthropogenic carbon dioxide (CO_2) emissions has harmed the global environment, causing severe pollution and climatic disruption. The sustainable conversion of CO_2 into value-added fuels is desirable for achieving carbon neutrality. Electrocatalytic CO_2 conversion is regarded as the most promising method for producing valuable-added fuels. Metal-organic frameworks (MOFs) with tunable structures, numerous active metal sites, and customizable pore sizes have recently emerged as efficient electrocatalysts for the selective conversion of CO_2 to carbonaceous fuels. The present review paper will concentrate on recent developments in the development of MOF and its related materials as electrode platforms for electrocatalytic CO_2 conversion processes. The selective electrocatalytic conversion of products from CO_2 to carbon monoxide (CO), methane (CH_4), and liquid fuels using MOF-based electrocatalysts is thoroughly explored. The higher current density, higher conversion efficiency, and excellent stability of MOF-based electrodes are mainly due to the synergetic combination of high surface area, and porous structure along active metal sites. Finally, the problems and prospects of MOF as an electrocatalyst are discussed to emphasize the efficient conversion of CO and other important products. This review is expected to provide a greater understanding of MOF as an electrocatalyst for the future development of CO_2 conversion on a larger scale.

1. Introduction

Rapid climatic changes on the planet have repeatedly indicated

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List of abbreviation

(CO_2)	Carbon dioxide
(MOFs)	Metal-organic frameworks
(CO)	Carbon monoxide
(CH_4)	Methane
(HCCOH)	Formic acid
(COFs)	Covalent organic frameworks
(ORR)	Oxygen reduction
(HER)	Hydrogen evolution
(OER)	Oxygen evolution
(FE)	Faradaic efficiency
(TOF)	turnover frequency
(SHE)	Standard hydrogen electrode
(V)	Volt
(NC)	Nanocrystal
(PMOF)	Porphyrin metal organic framework
(TMA)	Trimethylammonium
(RHE)	Reversible hydrogen electrode
(ZIF)	Zeolitic imidazolate framework
(DFT)	Density functional theory

variations in atmospheric composition, predominantly caused by CO_2 emissions (a primary C1 feedstock). Due to the burning of fossil fuels by man-made activities and natural volcanic eruptions, concentration levels of carbon emissions have increased tremendously and reached a record value of 417.06 ppm for partial pressure of CO_2 in the atmosphere in 2022 [1,2]. According to the global carbon budget, around 11 billion tons of CO_2 were emitted from fossil fuels during the 1960s and it is estimated to reach 37 billion tons of CO_2 per year (2.7 % annually) in 2022. Prolonged excessive increases in CO_2 levels can result in various issues, such as dissolution of CO_2 in coastal regions, decomposition of organic matter, and ultimately leading to the lowering of water temperatures [3,4]. In the meantime, to alleviate these issues and consider the rapid depletion of fossil fuels, the transformation of greenhouse CO_2 gas into valuable chemicals is essential to minimize global warming [5,6]. From another point of view, the research community no longer treats CO_2 as waste but as a valuable fuel source, contributing to large energy consumption requirements and helping to achieve a carbon-neutral cycle [7]. Fig. 1 shows an overview of the electrocatalytic CO_2 conversion into value-added fuel for various applications [8]. To achieve carbon neutrality, traditional methods involving CO_2 adsorption, activation, and subsequent conversion into desirable products remain challenging because of their poor transfer rate and low conversion efficiency [9,10]. Inspired by the evolution of nanomaterials, material chemists have developed various processes for the conversion of CO_2 using photocatalytic [11–13], electrocatalytic [14–16], thermo-catalytic [17–20], and biochemical pathways [21–23]. When compared to other catalytic methods, electrochemical conversion of CO_2 remains a promising and sustainable approach due to factors such as (i) low-cost and simpler operating techniques, (ii) desired products can be adjusted by changing operating conditions, which include operating potential, supporting electrolytes, and temperature, and (iii) high conversion efficiency and high stability.

As a result, the reduction and conversion of CO_2 into valuable fuels, categorized as various carbon C(number of carbon)-based products like C1 [CO, CH_4, HCOOH], C2 (ethanol, ethylene), C3 (propanol), through sustainable electrocatalytic methods are proven as efficient methods to reduce the CO_2 contamination in the environment [24–26]. Research efforts were established in the 19th century for the electrocatalytic

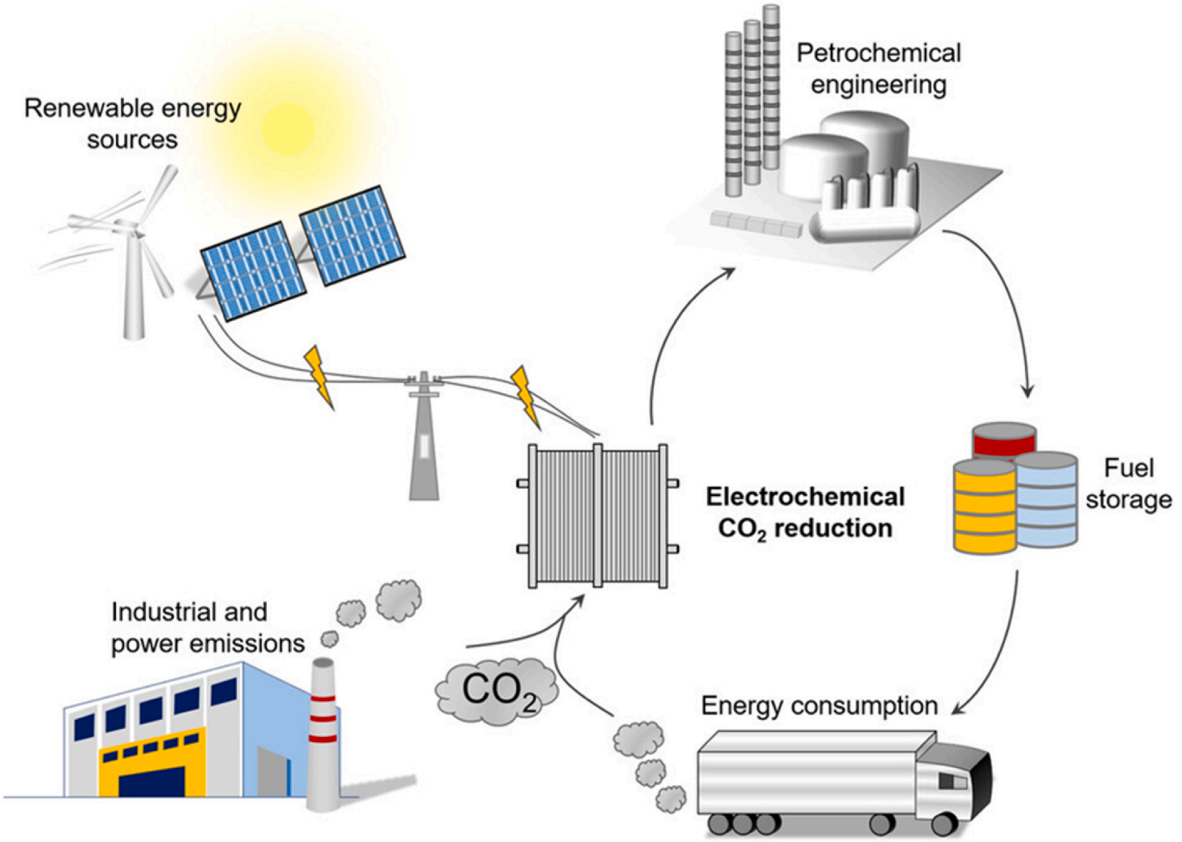


Fig. 1. An overview of electrocatalytic conversion of CO_2 into value-added fuels for various applications. Reproduced and Permission from **Ref.** [8]. Copyright 2021 John Wiley and Sons.

conversion of CO_2 to formate using amalgamated Zn as cathodes. Later, in the 1980s, various semiconductor (Ru, Mo) based electrodes were used for the conversion of CO_2 into alcohols. However, selective conversion to various desirable products with appreciable efficiency was greatly achieved using metallic copper-based electrodes. The electrochemical conversion reactions involving two electron/proton transfers for the formation of CO and formate can be achieved at lower potentials with higher faradaic efficiency [27–32]. On the other hand, the conversion reaction involving four electron/proton processes for the formation of CH_4 and alcohols requires larger overpotentials with poor selectivity [15]. Therefore, the search for efficient electrocatalysts that satisfy the operating potential, maximize faradaic efficiency, and ensure high selectivity is essential. Fig. 2 displays the electrochemical conversion of CO_2 to various carbonaceous products [33,34]. Numerous electrocatalysts such as transition metals (Cu, Fe) [35,36], noble nanomaterials (Ru, Pt, Ir), metal-free carbons, metal-organic frameworks (MOFs) [37,38], covalent organic frameworks (COF) [39,40], and single atoms [41–48] have been used for the electrochemical applications such as sensors and electrocatalytic reactions. Among them, MOFs which belong to the class of coordination polymers, are generally constructed from metal ions with nodes that are linked with organic ligands through a network arrangement and thus can be extended to gas storage, electrocatalysis, and electrochemical sensing applications. MOFs are a unique class of materials and shown as a superior conversion not only limited to CO_2 but also extended to H_2 evolution, O_2 reduction, methanol oxidation (fuel cell), and urea oxidation reaction (URR) [49,50] Besides pristine MOFs, by varying the medal nodes and the surrounding ligands, a large variety of MOFs are obtained which include bimetallic MOFs. The post-modification of pristine mono/bimetallic MOF via wet-chemistry or annealing process could lead to the formation of MOF-derived materials and MOF-supported single-atoms. The MOF and its derivatives have impressive properties such as high surface area, tunable size, controllable porosity, good chemical, and thermal stability. MOF-based materials have advantages compared to other electrocatalysts because they can be synthesized using cost-effective metals as metal nodes and thus the production cost in larger-scale industries can be enormously reduced.

Fig. 3 illustrates the significance of MOFs and their derivatives across a range of electrochemical applications. The figure highlights the versatility of MOFs in enhancing performance metrics such as energy storage, conversion efficiency, and catalytic activity, making them pivotal in advancing technologies like batteries, supercapacitors, fuel cells, and so on [51]. The strong application of MOFs in the electrocatalytic conversion of CO_2 mainly depends on the abundant active metal sites with a larger exposed active surface area, which increases the intrinsic properties of active metal sites. This unique property of MOF enhances the selective production of desired products from CO_2. Recently, a large number of reports on MOF-based electrocatalysts for the electrocatalytic as well as photocatalytic conversion of CO_2 have been developed. However, a comprehensive review that consolidates the recent progress specifically devoted to the electrocatalytic CO_2 conversion process and provides projections for future/ongoing research is still scarce in the literature. The review aims to selectively discuss the MOF-based materials towards electrocatalytic CO_2 conversion to various valuable fuels. We also discuss electrocatalytic principles and challenges faced by the electrocatalyst and provide solutions to achieve high conversion efficiency. An overview of various MOFs, bimetallic MOFs, MOF-derived carbon, and single-atom-catalysts from some of the reported electrocatalysts for conversion of CO_2 is explained. Finally, we discuss the future perspectives and the outcomes, which could leave a footprint, potentially witnessing the realization of a carbon-neutral cycle in the environment in the coming years.

2. Electrocatalytic principles and thermodynamics of CO_2 conversion

Structurally, CO_2 is a linear molecule (O═C═O) with a relatively shorter bond length (116.3 p.m.) and requires 800 kJ mol^{-1} of energy to dissociate C═O into various forms. Overall, the stable O═C═O structure is chemically inert and thus requires external energy under drastic conditions such as increasing temperature or pressure which is essential for CO_2 activation in chemical reactions. To meet the criteria, the electrocatalytic conversion of CO_2 offers various advantages, such as mild reaction conditions (e.g., pH), simple operating techniques, and good compatibility with sustainable energy sources. The experimental methods for the electrocatalytic reduction of CO_2 are typically carried out in an H-type cell using an electrocatalyst loaded with active materials as the working electrode, along with a reference electrode in one compartment, while a Pt counter electrode is placed in another compartment, which is separated by an ion-exchange membrane to avoid reoxidation of the products [52]. The key analytical parameters for assessing the electrocatalytic conversion of CO_2 are based on the

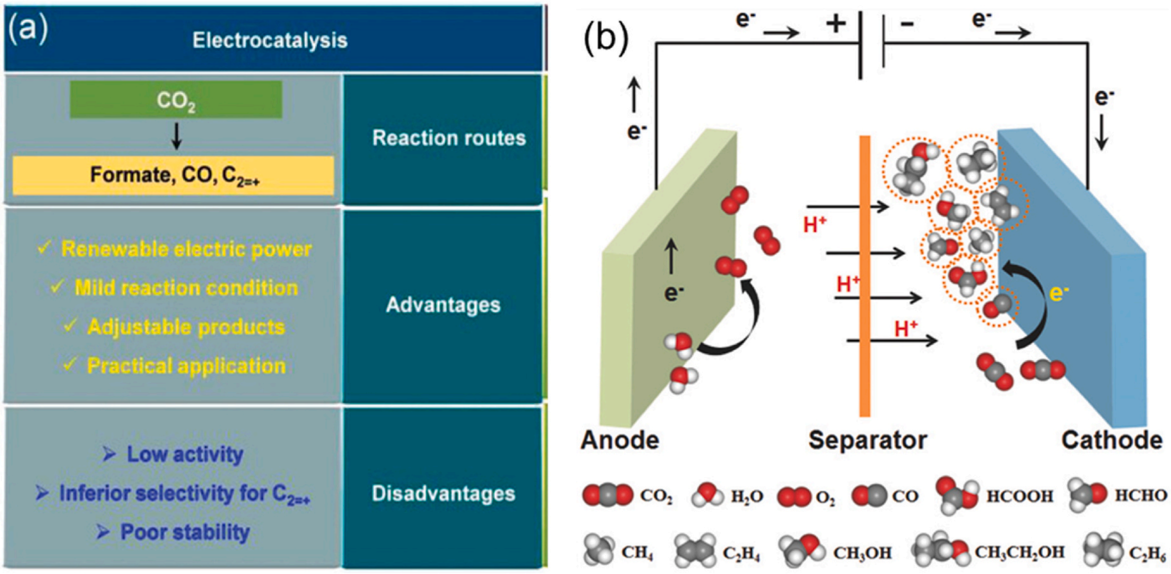


Fig. 2. Electrochemical pathway for conversion of CO_2 into carbonaceous fuels. Reproduced and Permission from **Refs.** [33,34]. Copyright 2018 and 2022 John Wiley and Sons.

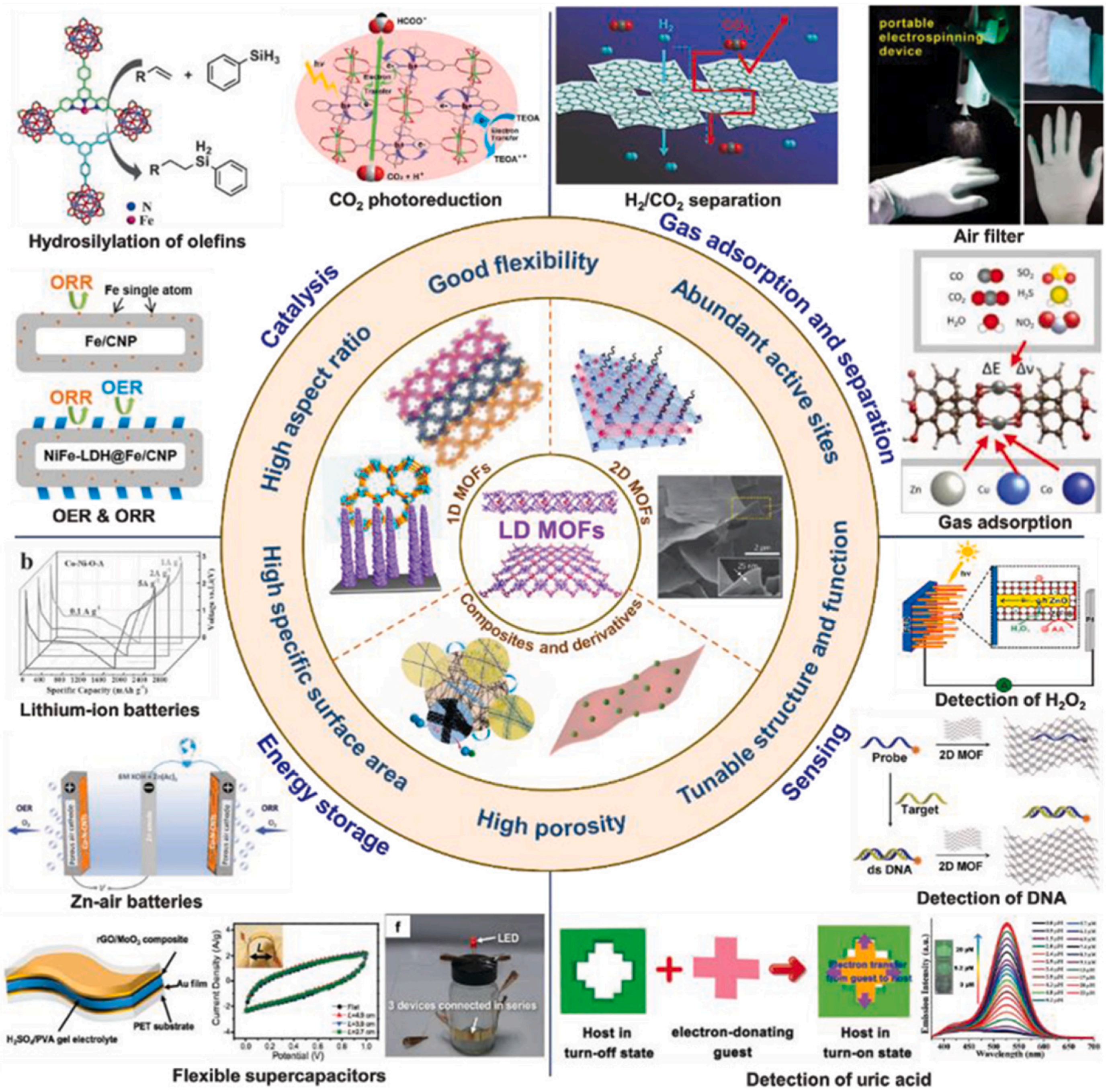
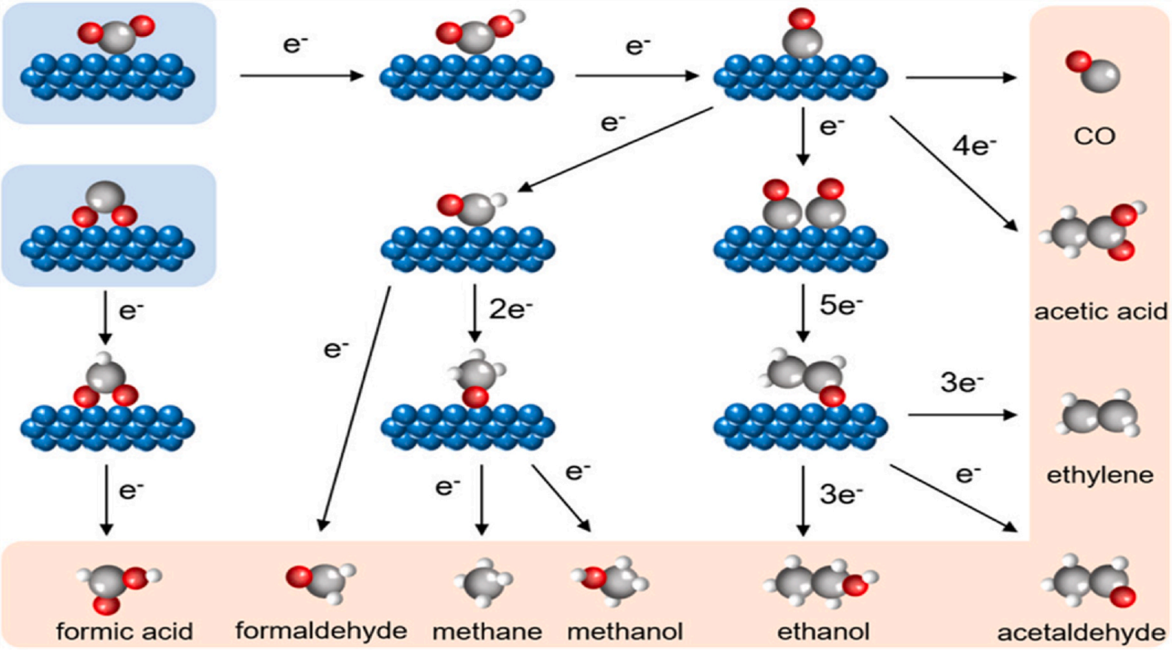


Fig. 3. Significance of MOF and its derivatives for various electrochemical applications. Reproduced and Permission from **Ref.** [51]. Copyright 2019 John Wiley and Sons.

following 1. onset potential, 2. high current density, 3. Faradaic efficiency (FE), and 4. turnover frequency (TOF). Typically, the electrocatalytic reduction of CO_2 multiple electron and proton transfer process and yields a variety of valuable gaseous and liquid products, including CO, formate, alcohols, hydrocarbons, and methane (CH_4), offering a sustainable route to producing alternative fuels. Generally, the CO_2 conversion process involves the following three steps: (i) chemisorption of CO_2 on the electrocatalyst surface, (ii) Dissociation of CO_2 molecules (C=O)/formation of C–H bond, and (iii) Desorption of molecules from the surface of the electrocatalyst. During the dissociation process, the CO_2 molecules are involved in the transfer of electrons/protons, resulting in the formation of various value-added products [53]. Initially, CO_2 can be reduced directly to obtain $CO_2^{\bullet -}$ (radical anion), which involves a single-electron process; but this reaction is highly unfavorable due to the large reduction potential of −1.9 V (vs. SHE) at neutral pH [54]. To avoid the formation of the radical anion, a large number of experimental strategies were carried out as shown in Fig. 4 [33].

Except for Equation (1), the remaining conversion reactions from the Equations are thermodynamically favorable. Equation (1) involves a single electron transfer process, which requires higher energy for activation of the CO_2 molecule, whereas the remaining electrochemical conversion processes involve multi-proton/electron transfers, making these reactions more feasible. Based on the above equations, it can be assumed that conversion reactions with less E^0 or with more positive values are thermodynamically favorable ($\Delta G = -nFE^0$). However, the



$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH \quad (1) \quad E^0 = -0.61\ V$$

$$CO_2 + 2H_2O + 2e^- \longrightarrow HCOOH^- + OH^- \quad (2) \quad E^0 = -1.49\ V$$

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O \quad (3) \quad E^0 = -0.53\ V$$

$$CO_2 + 2H_2O + 2e^- \longrightarrow CO + 2OH^- \quad (4) \quad E^0 = -1.34\ V$$

$$2CO_2 + 2H^+ + 2e^- \longrightarrow H_2C_2O_4 \quad (5) \quad E^0 = -0.91\ V$$

$$2CO_2 + 2e^- \longrightarrow C_2O^{2-}{}_4 \quad (6) \quad E^0 = -1.003\ V$$

$$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + H_2O \quad (7) \quad E^0 = -0.48\ V$$

$$CO_2 + 3H_2O + 4e^- \longrightarrow HCHO + 4OH^- \quad (8) \quad E^0 = -1.31\ V$$

$$CO_2 + 4H^+ + 4e^- \longrightarrow C + 2H_2O \quad (9) \quad E^0 = -0.2\ V$$

$$CO_2 + 2H_2O + 4e^- \longrightarrow C + 4OH^- \quad (10) \quad E^0 = -1.04\ V$$

$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O \quad (11) \quad E^0 = -0.38\ V$$

$$CO_2 + 5H_2O + 6e^- \longrightarrow CH_3OH + 6OH^- \quad (12) \quad E^0 = -1.22\ V$$

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O \quad (13) \quad E^0 = -0.24\ V$$

$$CO_2 + 6H_2O + 8e^- \longrightarrow CH_4 + 8OH^- \quad (14) \quad E^0 = -1.07\ V$$

$$2CO_2 + 12H^+ + 12e^- \longrightarrow C_2H_4 + 4H_2O \quad (15) \quad E^0 = -0.34\ V$$

$$2CO_2 + 8H_2O + 12e^- \longrightarrow C_2H_4 + 12OH^- \quad (16) \quad E^0 = -1.17\ V$$

$$2CO_2 + 12H^+ + 12e^- \longrightarrow C_2H_5OH + 3H_2O \quad (17) \quad E^0 = -0.32\ V$$

$$2CO_2 + 9H_2O + 12e^- \longrightarrow C_2H_5OH + 12OH^- \quad (18) \quad E^0 = -1.15\ V$$

$$2CO_2 + 14H^+ + 14e^- \longrightarrow C_2H_6OH + 4H_2O \quad (19) \quad E^0 = -0.27\ V$$

$$3CO_2 + 18H^+ + 18e^- \longrightarrow C_3H_7OH + H_2O \quad (20) \quad E^0 = -0.31\ V$$

$$2H^+ + 2e^- \longrightarrow H_2 \quad (21) \quad E^0 = -0.42\ V$$

Fig. 4. The electrocatalytic mechanism for the reduction of CO_2 into valuable products. Reproduced and Permission from **Ref.** [33]. Copyright 2018 John Wiley and Sons.

electrocatalytic conversion of CO_2 is not solely dependent on the thermodynamic barrier but also kinetically dependent, which affects the production rates.

3. Challenges associated with electrocatalytic reduction of CO_2

For both photocatalytic as well as electrocatalytic conversion of CO_2, the requirement of high conversion efficiency is the same, but the fundamentals of designing catalyst are different. MOFs are a unique class of materials that can work as both electrocatalysts as well as photocatalysts for the reduction of CO_2 with different mechanism pathways. In the case of photocatalytic conversion of CO_2, the atmospheric CO_2 is converted into solar fuels which are enabled by sunlight, and thus promising recyclability of CO_2 can be achieved. A large number of reports existed on using semiconductors as photosensitizers, and the potential ability of MOF has been expanded towards photocatalysts for the conversion of CO_2 [55,56]. Upon light irradiation, organic linkers in the excited state transfer the electrons to the metal node which promotes the charge separation process. However, the photocatalytic conversion efficiency is highly affected due to low visible light absorption and thus rapid recombination capabilities. In this regard, electrocatalytic conversion of CO_2 becomes a promising approach that involves (a) surface adsorption of CO_2 (b) electron transfer and proton migration, and (c) desorption of CO_2 from surface [57]. When compared with the photocatalytic method, the electrochemical pathway is promising towards practical applications due to its high conversion efficiency in scalable process. However, both photocatalytic and electrochemical methods have limited efficiency in larger-scale commercialization [58]. Electrochemical conversion of CO_2 into valuable fuels is considered a promising technology when compared to other conventional methods. Despite the valuable conversion of CO_2 using sustainable electrocatalytic methods, these approaches still face challenges in achieving practical conversions on a larger scale. Based on Fig. 4, a wide range of products can be obtained using multi-electron/proton transfer processes. However, the potential difference between these reactions is very small, making the selective formation of the desired products highly challenging. Another issue is that due to the slower diffusion ability of CO_2 molecules towards the electrocatalyst, it mainly results in low conversion efficiency. Most electrocatalytic conversion methods based on metallic copper (Cu) electrodes are affected by the accumulation of carbonaceous materials at larger current densities, resulting in poor stability. Over the past few decades, the rise of MOFs has outperformed various electrocatalytic reactions and replaced various transition metals [59,60]. For designing electrocatalytic conversion of CO_2, the electrocatalyst is required to convert CO_2 into valuable added fuels and chemicals with low cost and high conversion efficiency. Apart from MOF-based materials, the other well-known electrocatalysts are pure metal electrodes (Cu, Ni, Fe), Cu-based bimetals, metal-free carbon-based materials, layered double hydroxides, metal dichalogenides, 2D materials, single-atoms supported on matrices are proven as promising materials for electrocatalytic CO_2 reduction [61,62]. When a metal (building unit) is covalently connected with organic linkers consisting of nitrogen or carboxylic functional groups, MOF can be easily obtained. The majority of the MOFs reported methods belong to either hydrothermal or solvothermal processes [63]. Because to obtain high crystallinity with high thermal stability the reaction conditions for synthesis of MOF are extended up to 2 or 3 days. Although these techniques are time-consuming and synthesize MOF at a rapid duration or less consuming microwave irradiation, ultrasound irradiation processes are also employed [64]. In addition to the traditional methods some other emerging methods also exist in the literature which include laser-induced heating, Joule heating, and plasma heating process [65]. The adoption of various synthetic methods, a wide range of MOF, and its derivatives can be obtained as illustrated in Fig. 5. The diagram outlines the various MOFs and their derivatives adopted by various synthesis methods that could improve the electrocatalytic conversion reaction [66].

Some of the research groups are also devoted to studying the electrocatalytic reduction process of CO_2 using metal-free compounds namely COFs and CMPs, respectively. These metal-free conjugated polymers possess superior recycling ability due to the presence of cross-linked polymers as a structural unit), and large surface area can selectively adsorb CO_2 [67]. The utilization of COFs or CMPs even undergo an electrocatalytic reduction process to obtain CO only, however, the other carbon fuels are still scare because the formation of other hydrocarbons requires multi-electron/proton transfer processes are mainly mediated by active metal redox sites which are exclusively present in MOFs only. Therefore, MOFs are found to be advantageous in the electrocatalytic CO_2 reduction process when compared with COFs and CMPs.

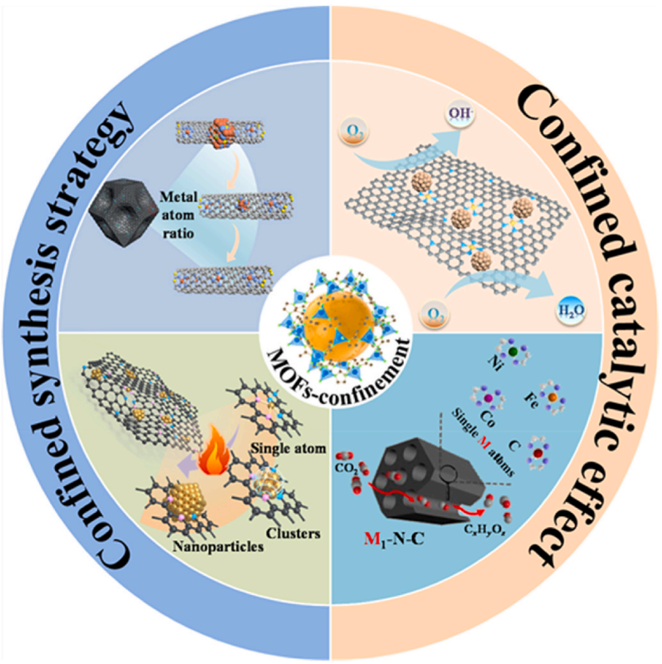


Fig. 5. Illustration of MOFs synthesis strategy and its electrocatalytic conversion towards CO_2. Reproduced and Permission from **Ref.** [66]. Copyright 2022 John Wiley and Sons.

The electrocatalytic reduction of CO_2 is highly challenging because the competitive proton involvement can lead to a wide range of carbonaceous products and therefore selectivity is the primary issue. In addition, the performance of CO_2 reduction can be affected by various parameters: 1. Overpotential, 2. high current density, 3. Tafel slope, 4. electrochemical surface area, 5. faradaic efficiency and 6. turn-over frequency. Due to the slow solubility of CO_2 in water the electrolyte pH, concentration and electrolytic cells are also to be analyzed. To overcome the above-mentioned issues, the formation of MOF-derived materials in which tuning of defects, composition of metals, porosity, and therefore adsorption energies of various reaction intermediates can be varied, as a result, high selectivity can be achieved.

4. MOFs based electrocatalyst for conversion of CO

MOFs are considered promising electrocatalysts for selective electroreduction of CO_2 in neutral pH conditions. In this regard, copper-based electrodes are well-known electrocatalysts, however, to exhibit selective reduction towards desirable products, tuning the morphology of Cu nanoparticles (electrodes) to less than 10 nm has been reported to deliver enhanced electrocatalytic activity. Kung et al., in 2017 [68] developed ultrafine copper nanoparticles (5 nm) decorated over Zr-MOF (NU-1000) on conducting substrate through solvothermal deposition and electrochemical reduction method. Among various materials, the Cu nanoparticles embedded into NU-1000 thin film showed a larger enhancement in the reduction current, with the observation of irreversible peak behavior that reflects the reduction of CO_2. At a constant operating potential of −0.82 V, both formate and CO are detectable; however, the faradaic efficiency of formate was found to be 31 %. In addition, the turnover number for formate and CO was reported as 47 and 4, respectively. Interestingly, the structure and composition of the electrocatalyst did not change even after the electrocatalytic conversion process, indicating that the metallic Cu embedded in the MOF network protects the electrocatalyst from decomposition. The combination of metallic nanocrystals linked with MOFs has been systematically proven to be electroactive and selective for the electrochemical reduction of CO_2.

4.1. Porphyrin-based MOF

Porphyrins belong to heterocyclic compounds, which are found in the form of hemoglobin, chlorophylls, cytochromes, and catalases, performing various functions in both humans and plants. Porphyrin is a unique class of macromolecular compounds with four pyrrole rings connected alternatively with methine linkage. Porphyrin linkers are involved in natural electrocatalysis with the presence of Cu or Fe for various oxidation and reduction reactions. Porphyrin complexes have been reported as molecular catalysts for electrocatalytic CO_2 conversions in non-aqueous medium, with higher catalytic activity observed in Fe(I/0) redox couple region after the addition of trifluoroethanol as an external proton source [69]. Porphyrins can coordinate with various transition metal ions to form porphyrin-based MOFs through a chelating effect. Recently, MOFs constructed with porphyrin as a ligand have received immense attention because of their structural and textural properties. Owing to the impressive chemical stability and rigidity offered by porphyrin, these ligand-based MOFs have been widely used in photochemical and electrochemical conversion reactions, such as CO_2 reduction. However, due to the poor conductivity of pristine porphyrin MOFs, efforts were made by Guntern et al., in 2019 [70], in which the interaction between colloidal nanocrystals (Ag NCs) and porphyrin MOFs to prepare Ag@Al-PMOF hybrids [Fig. 6(a)] played a significant role in improved electrocatalytic CO_2 reduction. Moreover, the size of synthesized spherical Ag NCs was 10.5 ± 1.4 nm with multiple-twinned structure, as presented in TEM images and TEM-EDX mapping confirmed the successful $Ag@Al_2O_3$ core@shell structure [Fig. 6(b–f)]. In addition, the Ag NCs are completely embedded in the Ag@Al-PMOF network, based on the TEM image [Fig. 6(g)]. It is reported that the incorporation of Ag NCs into porphyrin MOFs enhanced the selectivity for CO (55.8 %) along with other products, such as H_2 (gas) and formate (liquid), compared to Ag NCs alone. The design of an affordable electrocatalyst that can drive selective reduction of CO_2 to carbon monoxide with faradaic efficiency (100 %) is of urgent importance for the production of carbon-based liquid fuels. Shimoni et al. [71] developed Fe-porphyrin-based MOFs and achieved higher selectivity with a conversion rate of 100 % to CO mainly due to the presence of 3-carboxypropyl trimethylammonium (TMA), which produces electrostatic stabilization of CO intermediate when it becomes weakly bound on the surface. This might be due to the advantages of the 2D structure, which provides abundant active metal sites and permits the larger diffusion of CO_2 molecules towards the catalytic sites. Wang et al. [72] reported the MOF–NS–Co catalyst exhibits excellent performance in light-assisted CO_2 reduction. Under light irradiation, a large steep in the current response at −0.2 V in a CO_2-saturated electrolyte with a maximum current density of -16.8 mA cm^{-2} was reported at −1.05 V [Fig. 7(a)]. Whereas in the case of the absence of Co, the electrochemical response for MOF-NS lowers current densities, confirming that the presence of active Co atomic sites in the porphyrin unit facilitates electron transfer [Fig. 7(b)]. Furthermore, control experiments with N_2 instead of CO_2 show a more moderate current density, decreasing to −7.2 mA cm^{-2} highlighting the significant role of CO_2 [Fig. 7(c)]. The CO production rate for MOF–NS–Co under dark conditions rises from under visible light irradiation and reaches 640.3 mmol g^{-1} h^{-1} (−1.1 V) [Fig. 7(d)]. Long-term durability tests conducted at −0.6 V showed constant current density and stable faradaic efficiency (FECO) after 12 h of electrolysis, with negligible degradation (Fig. 7(e)). Additionally, the recyclability of MOF–NS–Co is supported by consistent FECO and jCO across four cycles [Fig. 7(f)].

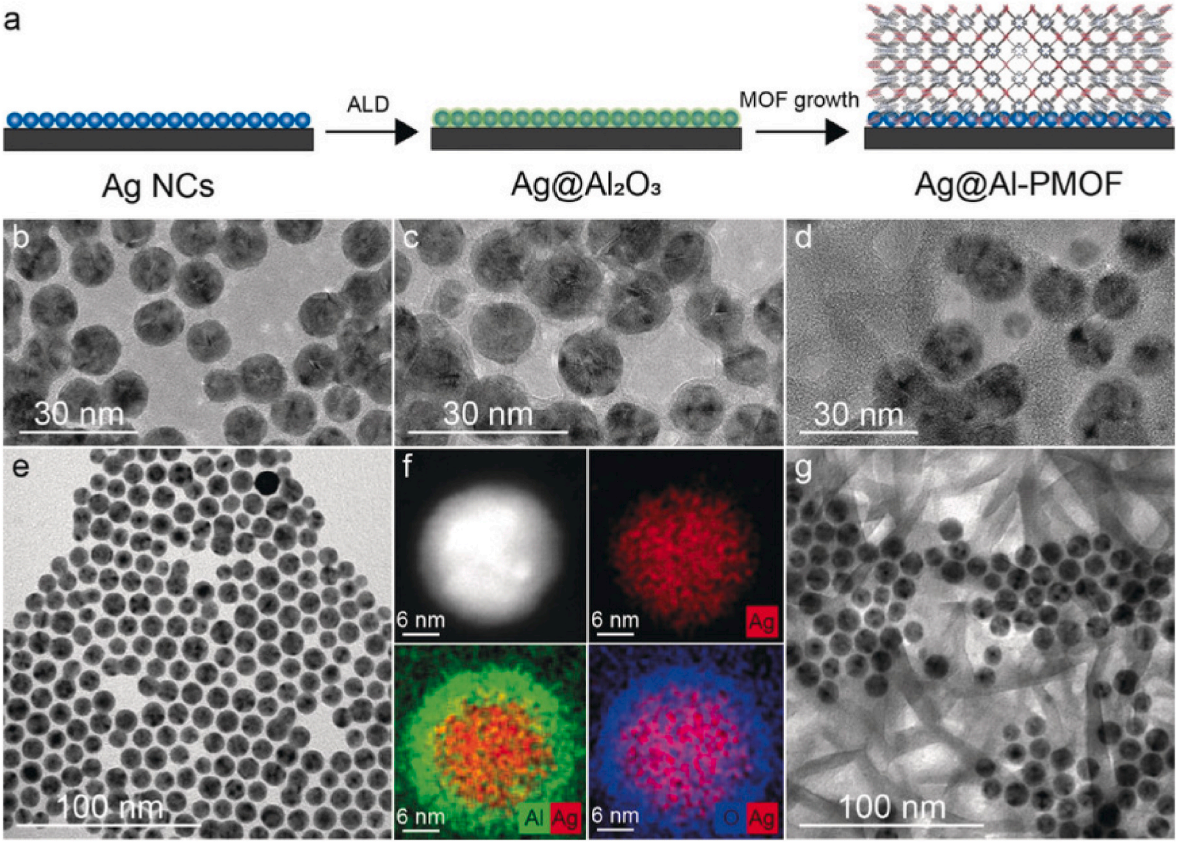


Fig. 6. Diagram illustrating the synthesis process of the Ag@Al-PMOF hybrid, (b, e) TEM images of Ag nanoclusters (NCs), (c, f) HAADF-STEM images of $Ag@Al_2O_3$ core-shell particles, and (d, g) TEM images of Ag@Al-PMOF hybrids. Reproduced and Permission from **Ref.** [70]. Copyright 2019 John Wiley and Sons.

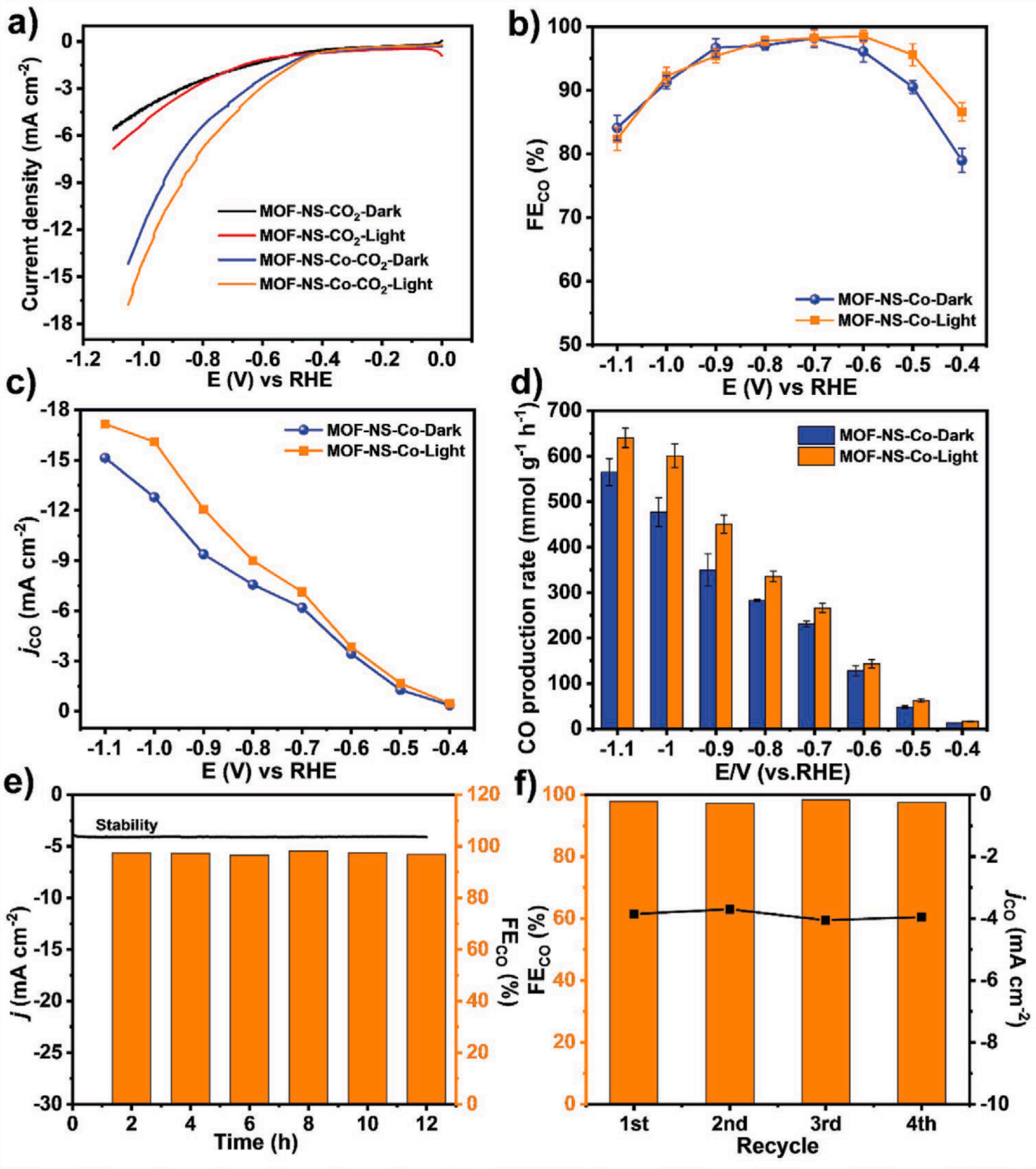


Fig. 7. (a) LSV curves of MOF-NS and MOF–NS–Co recorded in 0.1 M $KHCO_3$ saturated with CO_2 under both visible and black light. (b) FECO, (c) jCO, and (d) CO formation (e, f) Durability and recyclability tests under visible light at −0.6 V. Reproduced and Permission from **Ref.** [72]**.** Copyright 2021 John Wiley and Sons.

Wang's team recently developed Co NPs/MTPP (M = Fe, Co, and Ni) catalysts and found that Co NPs/FeTPP demonstrates an impressive potential range for electrocatalytic CO_2 reduction to CO. The catalyst achieved an efficiency of about 95.5 % at −0.82 V vs. RHE in an H cell and remains above 90 % within the range from −0.72 to −1.22 Vs RHE (Fig. 8) [73]. Gu et al. developed $Cu_2(CuTCPP)$ nanosheets and in the presence of 0.5 M $EMIMBF_4$ under CO_2-saturated CH_3CN, these Cu-MOF nanosheets exhibited significant activity, achieving an efficiency of 68.4 % for the formation of formate and 16.8 % for acetate [74]. Huang et al. developed cobalt-based MOFs integrated with viologen units using a self-assembly approach. The presence of viologen groups was used as electron-transfer mediators, which ultimately improves the electron-transfer ability thereby enhancing the activity of the CO_2 reduction reaction [75].

4.2. Transition metal-doped MOFs

The electrocatalytic performance of CO_2 is mainly affected by its intrinsic structure and morphology of MOF. Due to the non-conducting behavior of pristine MOFs, the MOFs can be tuned to become electrically conductive either through covalent interactions or doping with metal ions. The inclusion of a dopant on MOF could effectively enhance the surface area by rapidly creating defects and thus result in larger electrocatalytic activity when compared with pristine MOF. As previously discussed, the drawbacks of lower faradaic efficiency and poor adsorption capabilities are highly enhanced by the introduction of transition metals as dopants on its surface. Therefore, the resultant metal-ion-doped MOFs form versatile materials with chemical diversity. Cho et al. [76] have developed a facile synthesis route for doping various

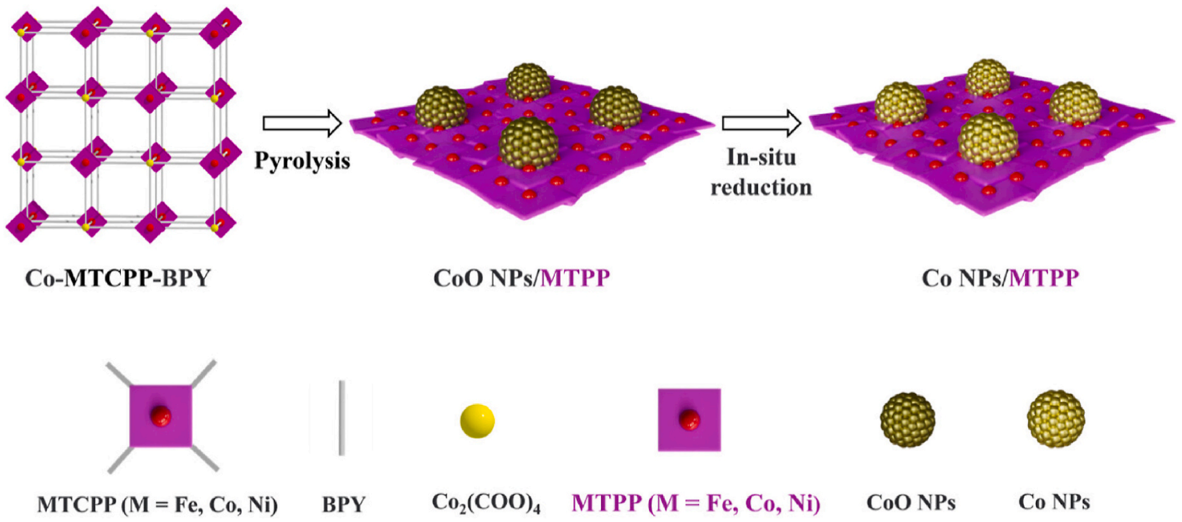


Fig. 8. Diagrammatic representation of the Co NPs/MTPP synthesis process (where M represents Fe, Co, or Ni). Reproduced and Permission from **Ref.** [73]. Copyright 2024 American Chemical Society.

transition metal ions (Ni, Fe, and Cu) into ZIF-8 for the selective formation of CO [Fig. 9]. Among these, the Cu^{2+} alters the electronic properties by causing a large decrease in the band gap. Therefore, the electrocatalytic reduction for CO_2 varies greatly between Fe^{2+} and Ni^{2+} doped systems. The performance of CO_2 reduction was studied using carbon paper as a working electrode, while the Pt counter electrode was separated by an H-type cell with a Nafion membrane in the presence of 0.5 M $KHCO_3$ as the electrolyte. The faradaic efficiency was estimated after 30 min of electrolysis, with the cathodic side of the H-type cell containing both gaseous and liquid products such as CO and H_2, respectively. It was found that Cu^{2+} doped ZIF-8 exhibited a higher current density and reached 11.5 mA cm^{-2}, whereas the undoped ZIF-8 and Ni^{2+} doped ZIF-8 exhibited lower current densities at −1.3 V in 0.5 M $KHCO_3$ (saturated CO_2) electrolyte. The observation of a low Tafel slope value indicates that CO_2 reduction is highly favorable on Cu^{2+} doped ZIF-8 for the formation of *COOH intermediate. This process

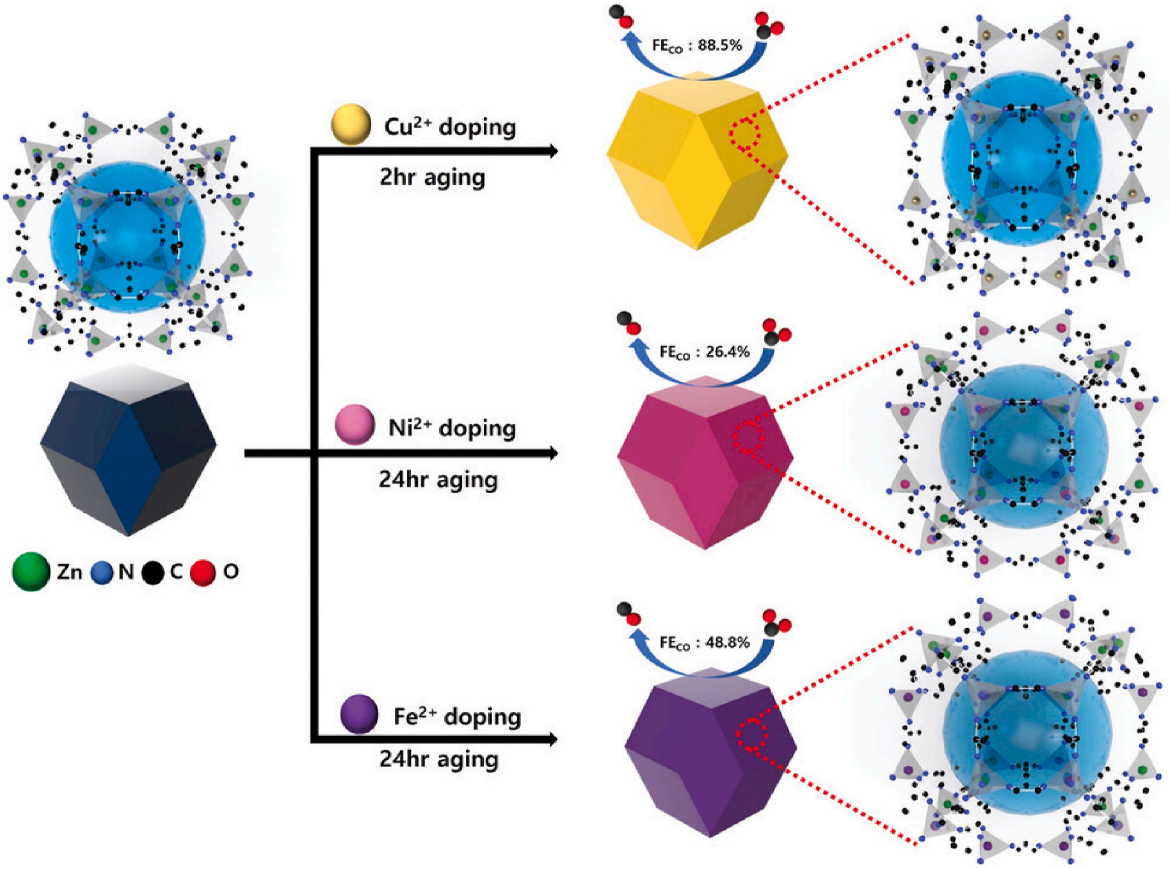


Fig. 9. Schematic Diagram depicting the synthesis process of the MxZny/ZIF-8 catalyst. Reproduced and Permission from **Ref.** [76]. Copyright 2023 John Wiley and Sons.

involves two proton and electron transfer steps, where the CO_2 molecule adsorbed on the surface is first protonated into *COOH intermediate. The intermediate is then further protonated at the next step, forming *CO, which eventually desorbs from the electrode surface. As a result, a high conversion efficiency of 88.5 % was obtained with Cu^{2+} doped ZIF-8 when electrolyzed at −1.0 V (vs. RHE).

4.3. Bimetallic MOF as electrocatalyst

The faradaic efficiency of electrocatalytic reduction of CO_2 is mainly affected due to the higher HER activity at larger negative potentials. To maximize the efficiency rate of the reaction, another alternative approach is to couple the MOF with two metals. The resultant bimetallic MOF can be able to enhance the efficiency rate and selectivity as well. It is reported that single-metallic Cu-based electrocatalysts mainly suffer from selectivity for CO formation, and thus significant efforts are still required to achieve the desired products. In this regard, bimetallic MOF-based electrocatalysts have been widely employed in catalytic conversion reactions because of their interesting combination of homogenous and heterogeneous properties. The presence of bimetallic centers in MOFs is particularly advantageous compared to pristine MOFs because it can improve the selectivity towards one specified valuable product with higher efficiency (>95 %). This enhanced selectivity is likely due to the presence of bimetallic centers, where one metallic center is responsible for tuning the high selectivity for CO, while the other metal center with a lower binding tendency towards CO generates H_2 at a larger production scale [60]. Taking advantage of bimetallic centers, Zhang et al. [77] developed a 2D- MOF in which zinc dihydroxy complex was linked with copper phthalocyanine for high selective CO conversion. The electrocatalytic studies conducted in the presence of 0.1 M $KHCO_3$ reported high selectivity towards the formation of CO with a FE of about 88 %, along with long-term durability of more than 10 h, which was found to be higher than pristine MOF-based electrocatalysts. The high electrocatalytic activity toward the reduction of CO_2 is due to the synergetic effect of CuN_4 and ZnO_4 present in 2D-MOF. Inspired by the Fischer-Tropsch synthesis process, which involves a Cu-based catalyst for high selectivity, Xu et al. [78] have engineered CuIn-based bimetallic MOFs for the conversion of CO_2 into CO selectively [Fig. 10]. Under an optimized mole ratio of CuIn-MOFs (3:1), the electrocatalytic studies reported a good faradaic efficiency for the conversion of CO (78. 6 %) and formate (48.4 %) with long-term durability of about 6 h when $KHCO_3$ was used as electrolyte.

4.4. MOF-derived electrocatalyst

The above discussions are mainly based on pristine MOFs as electrocatalysts for the selective conversion of CO. However, these pristine MOF-based materials show lower activity compared to other inorganic materials because of their intrinsic poor conductivity and low structural durability. In pristine MOF, the stability of the electrocatalyst is mainly affected by the presence of trace impurities in electrolyte covers the active surface area and thus the electron transfer at the interface towards CO_2 is strongly affected [79,80]. Moreover, the pristine MOF undergoes structural changes in harsh electrolyte conditions as a result agglomeration and loss of active metal sites are possible. To achieve longer stability, the pristine MOF was subjected to a thermal annealing or acid etching process to obtain MOF-derived carbon or MOF, and its derivatives can be formed. This post-treatment process of MOF helps improve conductivity by uniformly distributing active metal sites, facilitating rapid charge transfer from the electrode. As a result, a higher current density and maximum faradaic efficiency with high selectivity can be achieved through the selective conversion of CO using MOF-derived materials demonstrated by Wang et al. [81] reported that through the in-situ formation of Ag electrode (ER-AF) obtained from Ag-MOF by applying a constant voltage of −1.3 V for 30 min. The CO_2 reduction performance for ER-AF in the presence of 0.1 M $KHCO_3$ exhibited a less positive onset potential of about 420 mV with higher current densities compared to pristine Ag MOF. MOF precursors can be converted into MOF-derived materials due to factors such as increasing active metal sites by tuning composition through synthesis protocols, which improves conductivity and large surface area as reported by Zhang et al. [82] developed MOF-derived Ni on N-doped porous carbon as an electrocatalyst for the selective conversion of CO [Fig. 11]. The presence of CTAB as a modifier enables greater adsorption of Ni^{2+} ions on the surface of ZIF-MOF, and after the pyrolysis process, it was converted into porous carbon. The electrocatalyst also demonstrated 98 % conversion efficiency at −0.7 V, outperforming other Ni-based electrocatalysts.

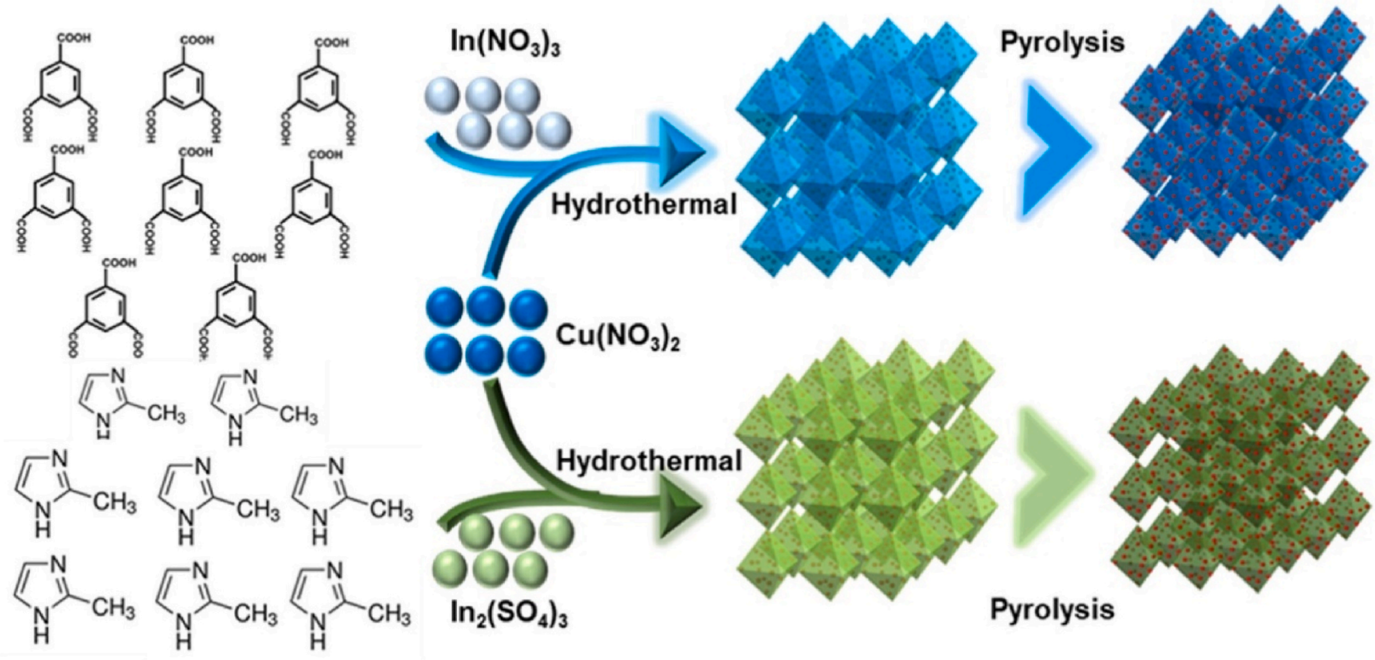


Fig. 10. Illustration of the CuIn-MOF catalyst synthesis process. Reproduced and Permission from **Ref.** [77]. Copyright 2020 Springer Nature.

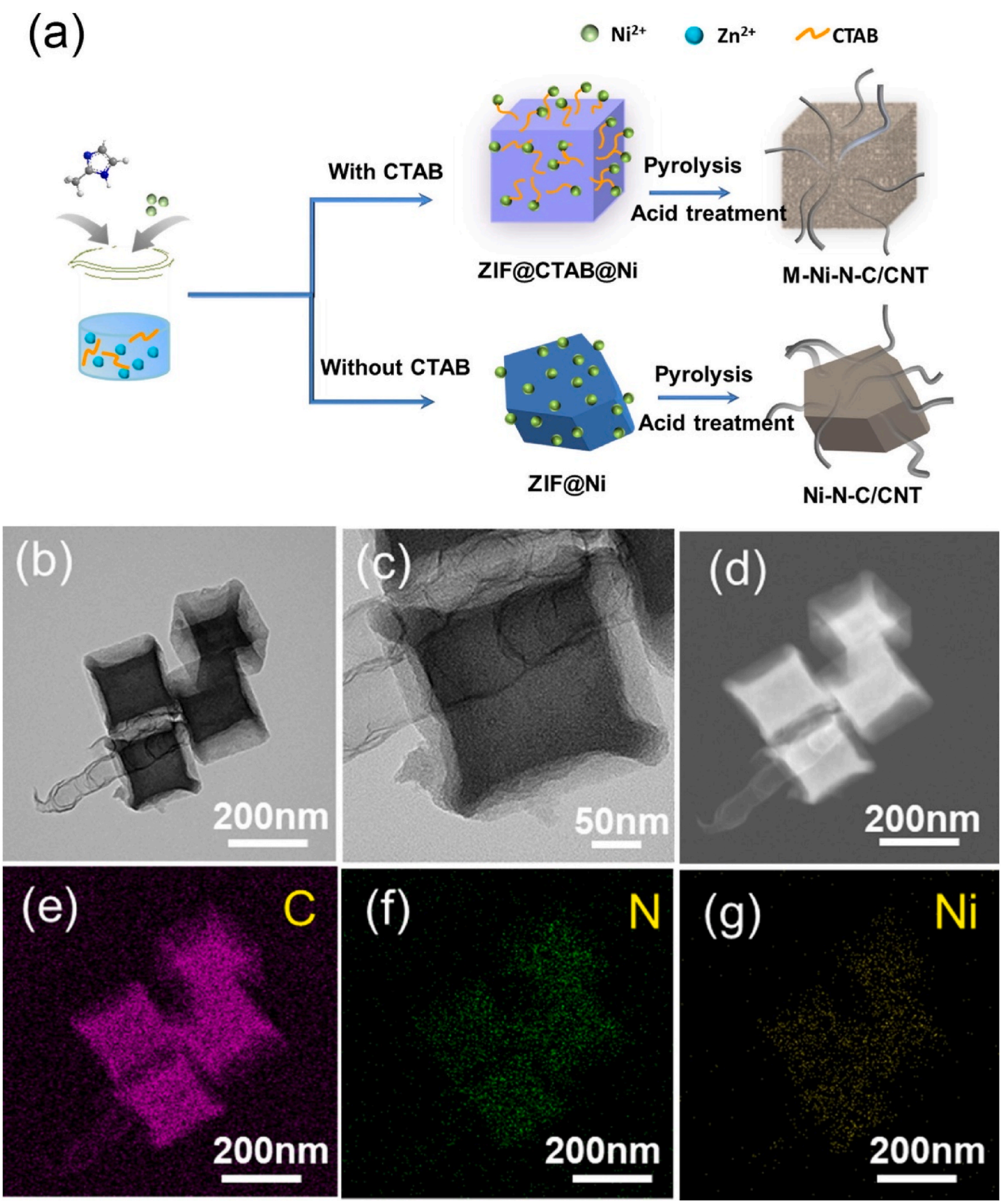


Fig. 11. (a) Schematic representation of the synthesis approach for MNiANACAx/CNTs and NiANAC/CNTs, (b, c) TEM images, and (d–g) HAADF-STEM images of MNiANACA2/CNTs. Reproduced and Permission from **Ref.** [82]. Copyright 2023 Elsevier.

4.5. *Single-atoms on MOF as electrocatalyst*

Recently, tailoring the coordination sites with single atoms has emerged as an efficient approach for enhancing efficiency and selectivity in electrocatalysis because of their unique electronic structure and high atomic utilization. Single-atoms or single-atom alloys are an emerging class of materials in which transition atoms dispersed on the surface do not interact with each other and the presence of single-atomic sites provides 100 % selectivity which is different from nanomaterials and nanoclusters. In this regard, the atomically dispersed metal atoms on the surface of MOF act as hosts could lower the activation barrier and thus ultimately enhance the catalytic activity. Zhang et al. [83] designed a single-atom-based electrocatalyst in which Bi atoms were derived after the pyrolysis of Bi-MOF [Fig. 12]. Also, the reported atomically dispersed Bi atoms on MOF exhibited electrocatalytic activity towards CO_2 and were highly selective CO formation with maximum faradaic efficiency. The resultant Bi single atoms dispersed on N-doped carbon exhibited a higher current density located at −0.5 V (with reference to RHE) and these values were much higher than those of Bi clusters on N-doped carbon and Bi nanoparticles on N-doped carbon along with higher TOFs of 535 h^{-1} and 10118 h^{-1} at −0.39 V and −0.58 V, respectively. The decoration of single atoms and MOF carbonization can

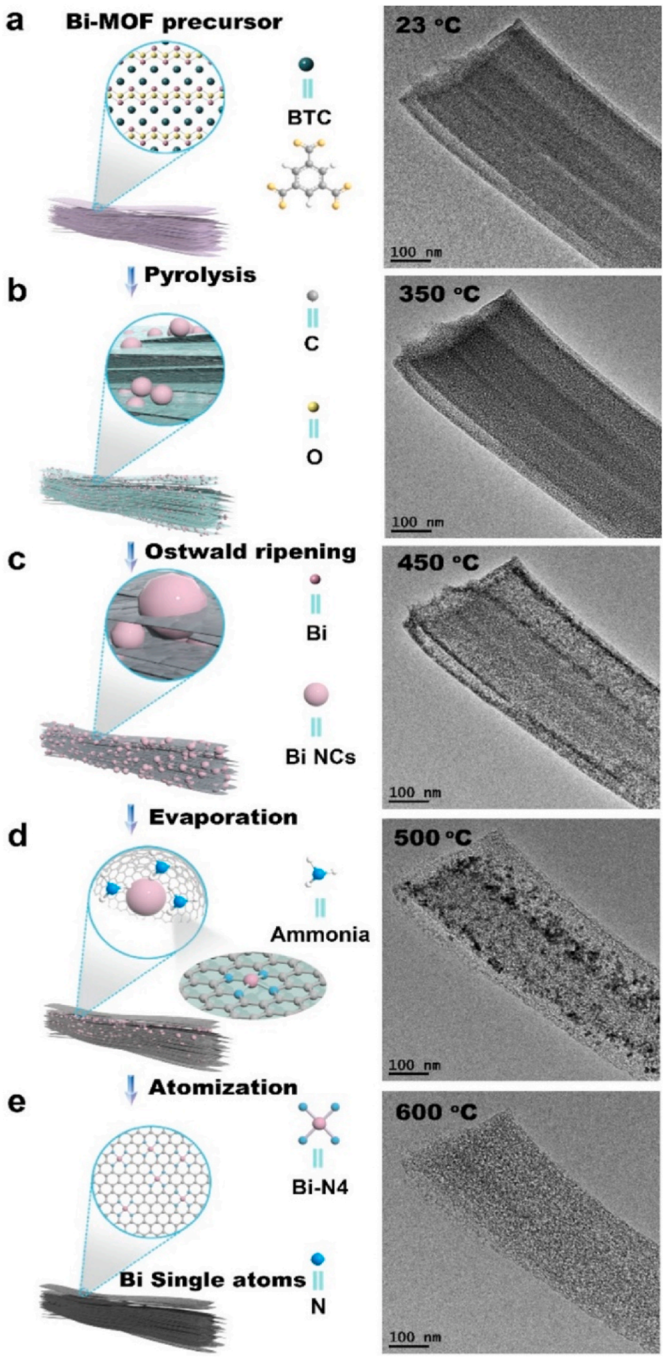


Fig. 12. (a–e) Diagram illustrating the transformation of Bi-MOF into single Bi atoms, along with representative TEM images of Bi-MOF pyrolyzed at different temperatures using DCD in situ. Reproduced and Permission from **Ref.** [83]. Copyright 2019 American Chemical Society.

be decoupled from each other during pyrolysis, which is one of the promising methods for the modulation of single atoms in a MOF environment. In this regard, Zhang et al. [84] reported the rational decoration insertion of Ni atoms by replacing the Zn, which was linked with N-doped carbon, due to the weak bond strength between Zn coordinated with N-dope carbon in an acidic medium [Fig. 13]. Under optimized conditions, Ni atoms were linked to 3- nitrogen atoms in the porous carbon network, demonstrating a higher conversion efficiency (95.6 %) and achieved TOF (1425 h^{-1}) at −0.65 V. This implies that the Ni–N_3–C electrocatalyst reduces the rate determination step, and improves the electrochemical conversion of CO_2 into CO.

5. MOF-based electrocatalyst for conversion of acids

Electrocatalytic CO_2 reduction can produce various products such as CO, formate, alcohols, and hydrocarbons through multi-proton/electron transfer processes. Compared to other desired products, the formation of acids (HCOOH) is a primary feedstock for the synthesis of various chemicals and is also used as an H_2 energy carrier in liquid fuels. In the search for an efficient catalyst for selective conversion of COOJ, Sn-based catalysts act as electrocatalysts with higher conversion efficiency at lower operating potentials. This review mainly discusses the importance of MOFs as electrocatalysts for the reduction of CO_2, Geng et al. [85] reported Sn-doped ZIF-8 for the selective formation of formic acid. The Sn-doped ZIF-8-based electrocatalyst underwent potentiostatic electrolysis and revealed that both CO and COOH were produced starting at −0.5 V vs. RHE, whereas the selective formation of COOH was observed at −1.1 V vs. RHE. A similar investigation was performed on ZIF-8 alone, but it was found that only CO formed in all the potential regions from −0.4 to −1.3 V vs. RHE, strongly indicating the role of Sn as a dopant on ZIF-8 for the production of formic acid. Due to the presence of low active Zn nodes in ZIF-8, the CO_2 adsorption capability is limited. On the other hand, the competitive reaction for the formation of H_2 is significantly enhanced. However, the faradaic efficiency for the formation of HCOOH is 47 %, and the competitive HER is about 28 %. The formation of HCOOH is mainly due to the presence of Sn nodes, which induce the formation of the formate intermediate through a lower energy barrier and increase the efficiency of HCOOH formation. A similar investigation was conducted by Deng et al. [86] using Sn-based MOF (with a coordination number of Sn of 6) for the electrocatalytic reduction of CO_2 to formic acid. The higher efficiency for formic acid formation using Sn-based MOFs is due to the adsorbed CO_2 molecules on the electrocatalyst, which generate a carbon dioxide anion radical, and this adsorbed radical anion is further activated to form a formate radical anion through an electron-coupled proton transfer process. As a result, the faradaic conversion efficiency for the formation of formate is about 85 %. The increased performance of Sn-based MOFs as electrocatalysts were demonstrated by Wang et al. [87] in 2022, and they found that the faradaic efficiency was further enhanced with Sn-MOF, reaching up to 92 %. The authors reported that the stronger interaction between Sn metal nodes and the formate anion enhances the formation of formic acid at a potential of −1.2 V vs. RHE, achieving around 20 mA cm^{-2} current density.

5.1. MOF-derived electrocatalyst

Another class of metals, namely Bismuth (Bi), is also widely used for the selective conversion of CO_2 into formic acid. The choice of Bi-based MOF-derived electrocatalyst was explored as an alternative to Bi metals, offering increased surface area and high carbon ratio, which enhances conductivity, thereby significantly improving electrochemical selectivity. Avila-Bolívar et al. [88] have developed Bi-MOF-derived N-doped carbon hybrids as electrocatalysts for the selective formation of HCOOH. Based on DFT and experimental results, the presence of Bi in the MOF-derived unit played a crucial role in the selective formation of HCOOH, yielding high conversion efficiency. Takaoka et al. [89] also developed a combination of MOF (UiO-66) and Bi as an electrocatalyst, and the current density was found to be four times higher than that of pristine UiO-66 and bare Bi, respectively. These findings suggest that the presence of Bi enhances the CO_2 conversion rate.

6. MOF-based electrocatalyst for conversion of alcohols

The conversion of CO_2 into liquid fuels, such as methanol, is of great importance because of its higher energy density and its potential as an alternative substitute fuel for vehicles. The conversion of CO_2 into methanol requires a six-electron/proton process and is therefore considered to have slow electron transfer kinetics compared to CO

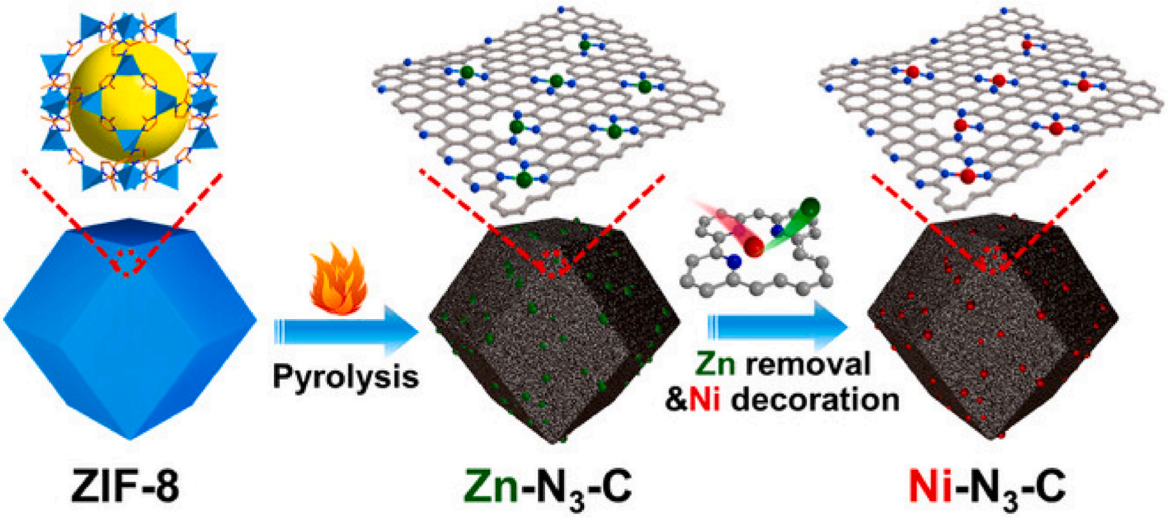


Fig. 13. Low-coordination single-atom Ni electrocatalysts synthesized through the PSMS technique. Reproduced and Permission from **Ref.** [84]. Copyright 2021 John Wiley and Sons.

formation. Numerous reports exist in the literature on copper-based -metallic electrodes for the electrocatalytic conversion of CO_2 into methanol; however, the selective formation of methanol remains a significant issue. To meet the criteria, MOF-based electrocatalysts are highly advantageous because of their unique physical and chemical properties, which offer high selectivity towards CO_2 reduction. Inspired by the selectivity offered by copper metallic electrodes, Cu-MOF electrocatalysts with porous structures and abundant active metal sites are an ideal choice to meet the requirements for high selectivity. Albo et al. [90] designed Cu-MOF-based gas diffusion electrodes with a large surface area and a high abundance of Cu metal centers, facilitating the selective formation of methanol from CO_2 electrocatalytic reduction. The experimental results report a higher faradaic efficiency of 16 % for about 12 h. The use of MOF as an electrocatalyst for CO_2 reduction offers several advantages, such as (i) minimized H_2 generation (ii) large faradaic efficiency, and (iii) long-term durability. However, pristine Cu-MOFs are poorly electrically conductive, and therefore, the conversion of organic ligands in MOF units into porous carbon materials has been shown to enhance the conductivity and thus significantly improve selectivity. Yang et al. [91] reported MOF-derived Cu/Cu_2O-based electrocatalyst, where the presence of Cu/Cu_2O interface exhibited weaker adsorption ability towards *CO, while the surface of Cu_2O has stronger binding energy with *H, inducing the selective formation of CH_3OH. The greater adsorption ability of *H for Cu/Cu_2O might be due to the presence of a thin hydroxide layer on its surface. At a lower overpotential of about −0.7 V, the Cu/Cu_2O-based MOF-derived electrocatalyst was reported to provide a faradaic efficiency of about 45 %, which is higher than that of pristine Cu-MOF. Liao's team has developed a novel MOF named CuSn–HAB, which features heterodimetal dual sites consisting of Sn and Cu. These dual sites include two SnN_2O_2 units and CuN_4 units, connected through μ-N atoms, and the structure of CuSn–HAB confirmed through SEM and TEM images, as illustrated in Fig. 14 [92]. This MOF demonstrated a low potential of −0.57 V (vs RHE) and exhibited an impressive Faradaic efficiency (FE) of 56 % for eCO_2RR, outperforming alcohols (ethanol). Table 1 provides a comprehensive comparison of different MOF-based electrocatalysts used for the selective reduction of various CO_2-derived products. The table highlights the performance metrics of each catalyst, including product selectivity, efficiency, and reaction conditions, offering a detailed overview of how these catalysts facilitate the electrochemical reduction of CO_2 into specific products such as CO, formate, alcohols, and hydrocarbons. This comparison underscores the versatility and effectiveness of MOF-based electrocatalysts in achieving targeted and efficient CO_2 conversion.

7. MOF@ COF-based materials for conversion of CO_2

Another class of porous crystalline polymeric frameworks made up of metal-free (organic) molecules are formed by strong covalent bonds, known as covalent organic frameworks (COFs) offer good durability and are also reported with good selectivity as line MOFs. Individually, MOFs and COFs are reported as having high efficacy towards photocatalytic and electrocatalytic processes, however, the performance is not satisfactory due to monotonous assemblies. In this regard attempts are made by incorporating MOF into COF could enable diversifying properties because of their similarity in structure along with exceptional synergetic features. Considering an example, the presence of amino groups in MOF could be able to form imine bonds with aldehyde groups in COFs using Schiff base reaction, to form MOF@COF-based hybrid material. In this regard, a large number of MOF@COF can be synthesized by tuning the functional groups between MOFs and COFs which can offer intrinsic properties such as high chemical stability with good crystallization. Therefore, it is believed that in combination of MOF@COF as a composite porous framework could improve the electrocatalytic activity towards CO2 reduction reaction. However, few reports based on MOF@COF towards electrochemical reduction of CO_2 have existed in the literature [93].

8. Conclusion and future perspectives

In conclusion, MOF and its derived materials have exhibited outstanding electrocatalytic performance toward the reduction of CO_2 into variable hydrocarbon fuels such as CO, formic acid, and methane. The promising performance delivered by MOF and its derived materials have the following unique properties: (i) high surface area favors the exposure of abundant active metal sites in $KHCO_3$, (ii) tunable porosity enables rapid electron transfer and mass transport of electrolytes, (iii) tailorable 3D structure facilitates surface functionalization with various linkers with various shapes and (iv) diverse composition improves synergetic interaction with multi/hetero atoms which reduces the overpotential for reduction of CO_2. Benefiting from the advantages of higher surface area, rich and active metal sites, tunable porosity, and compositional modularity, these materials facilitate rapid electron transfer, stronger adsorption sites, and enhanced desorption ability the MOFs served as a promising place as a potential replacement for precious metallic electrodes in the electrocatalytic conversion of CO_2

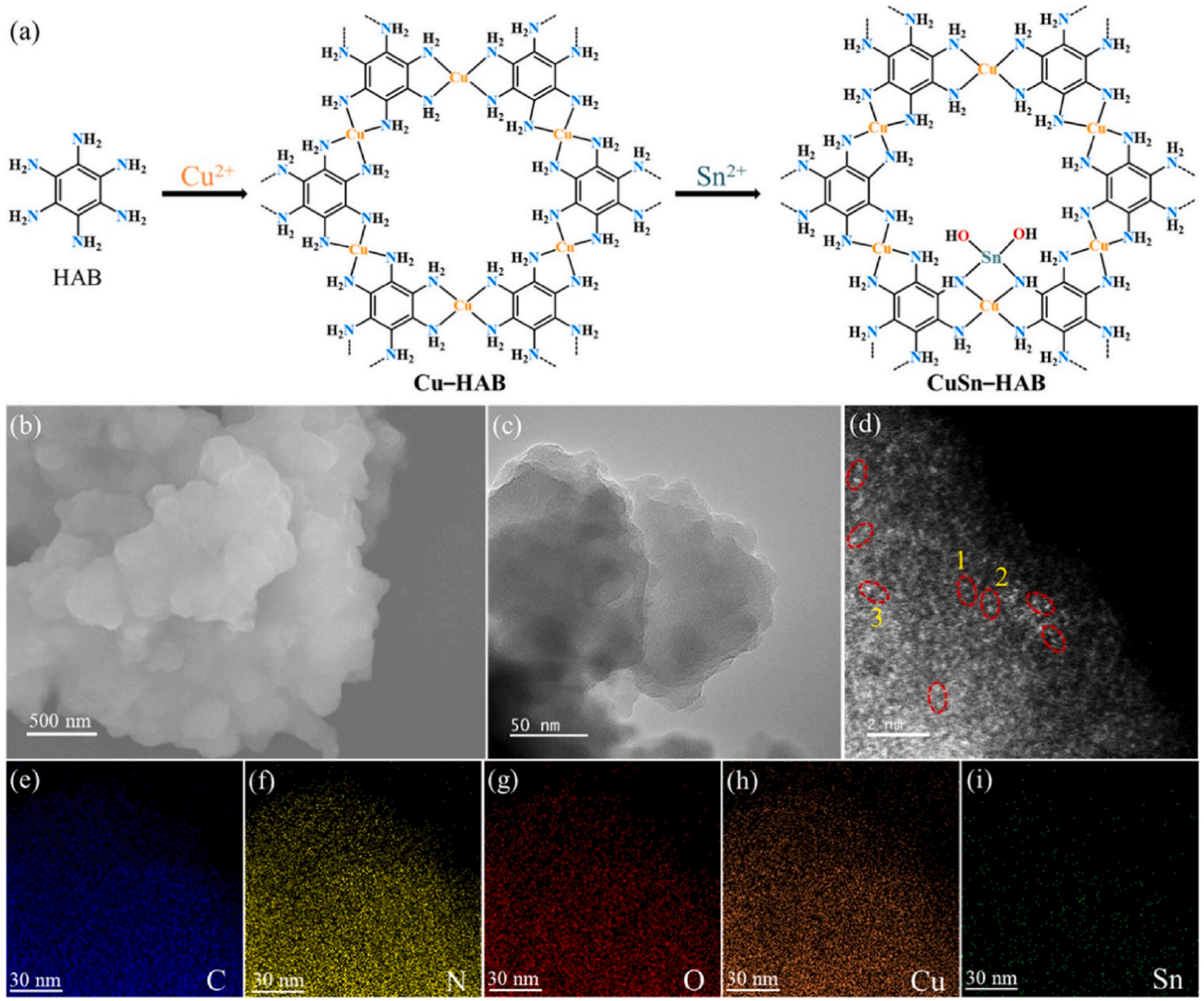


Fig. 14. (a) Schematic representation of the synthetic protocol for CuSn–HAB preparation. Images of CuSn–HAB include (b) SEM, (c) TEM, (d) AC-HAADF-STEM, and (e) EDX analysis. Reproduced and Permission from **Ref.** [92]. Copyright 2023 American Chemical Society.

into valuable products. On the other hand, MOFs and their derivatives show strong improvement in electrical conductivity along with the rich abundance of doped porous carbon (heteroatom doped) are responsible for high conversion efficiency with larger improvement in selectivity formation of carbon fuels. These collective inherent properties of MOF and its derivatives resulted in the effective conversion of CO_2 into desired products with good efficiency and long-term stability. With strong holding of numerous advantages, not only MOF-based electrodes, but the majority of the reported electrodes are also facing several challenges in the selective conversion of products: (i) limited selectivity, as explained in the mechanism (Fig. 4) the electrocatalytic reduction process involves a multi-proton/electron transfer process with a complicated reaction pathway and leads to poor selectivity. At −1.12 V (Vs. SHE) the CO_2 gets reduced into CO and HCOO- ions to form methanol. However, at a slightly higher potential (−1.35 V vs. SHE), the formation of hydrocarbons becomes dominant, as a result, selectivity is among the big challenges in conversion reactions, (ii) limited efficiency, the electrocatalytic reduction was carried out in an aqueous medium and therefore the competence of HER also dominant at higher negative potentials, as a result, the faradaic efficiency rate is another challenge. Particularly MOF-based catalysts and (iii) structural stability, as an electrocatalyst was subjected to harsh conditions (acidic or neutral), the MOF undergoes structural changes, and therefore durability is another challenging issue in MOF-based electrocatalysts. Taking into consideration the challenges faced by electrocatalysts, the MOF-based electrodes require less attention in the future (i) prediction of reduction mechanism pathways in experimental conditions for theoretical calculations, (ii) the selectivity and efficiency could be improved by appropriately selecting active metal centers or decorating the MOF with metal nanoparticles and also choosing conjugated ligands to improve the electron transfer rate, and (iii) the stability of the MOF could be improved by functionalization with corrosive resistant ligands, MOF on MOF growth, MOF based composites. Overall, developing MOF-based materials that possess high conductivity, superior catalytic activity, and good stability is highly important in the future.

CRediT authorship contribution statement

E. Sivasurya: Writing – original draft. **Raji Atchudan:** Writing – original draft. **Mohamed Gamal Mohamed:** Writing – review & editing,

Table 1
Comparison of different MOF-based electrocatalysts for selective reduction toward various target products.

Electrocatalyst	Selectivity Product	Electrolyte	Operating potential	Faradaic Efficiency	Stability	References
Cu-SIM NU-1000 thin-film	CO	1.1 M $NaClO_4$ (pH- 4.6)	−0.82 V vs. RHE	30 %	–	[68]
Ag-doped Co_3O_4 catalyst	CO	0.1 M $KHCO_3$	−1.8 V vs. SCE	21.33 %	10 h	[94]
MOF/AuNME	CO	0.1 M $KHCO_3$	−1.0 V vs. RHE	15.7 %	1 h	[95]
Bi–N_4 sites on porous carbon	CO	0.1 M $NaHCO_3$	0.39 V vs. RHE	97 %	4 h	[83]
Ni–N-doped porous interconnected carbon	CO	0.5 M $KHCO_3$	−0.65 V vs. RHE	95.1 %	24 h	[96]
Ag@Al-PMOF	CO	0.1 M $KHCO_3$	−1.1 V vs. RHE	55.8 %	12 h	[70]
PcCu-O_8-Zn	CO	0.1 M $KHCO_3$	−0.7 V vs. RHE	88	>10 h	[77]
UiO-66-B_TMA	CO	0.1 M $NaHCO_3$	−0.8 V vs. RHE	89 %	5 h	[97]
Ni-Nx-C	CO	0.5 M $KHCO_3$	−0.65 V	95.6 %	10 h	[84]
Cu0.5Zn0.5/ZIF-8	CO	0.5 $KHCO_3$	−1.0 V vs. RHE	88.5 %	6 h	[76]
K-defect-C	CO	0.5 $KHCO_3$	−0.45 V	99 %	10 h	[98]
Ag-MOF on Ag foam	CO	0.1 M $KHCO_3$	−1.15 V vs. RHE	91. 2 %	12 h	[81]
CuIn-MOF	**CO**	**0.5 M $KHCO_3$**	**0.86 V vs. RHE**	**78.6 %**	**6 h**	[78]
Cu/Ni/Zn-MOF	**CO**	**0.1 M $KHCO_3$**	**−0.6 V**	**99.7 %**	**48 h**	[99]
MOF-residing Fe-porphyrin	**CO**	**0.01 M $LiClO_4$**	**−1.3 V vs. NHE**	**100 %**	**–**	[71]
g-C_3N_4@Co-(Co + Cu)PMOF	**CO**	**0.1 M $KHCO_3$**	**−1.4 V**	**97.8 %**	**12 h**	[100]
MOF-derived NiANAC	**CO**	**0.1 M $KHCO_3$**	**−0.7 V vs. RHE**	**80 %**	**20 h**	[82]
Zeoliticimidazolate framework-8 (ZIF8)	**HCOOH**	**0.5 M $KHCO_3$**	**−1.1 V**	**74 %**	**–**	[85]
Bi_2CuO_4	**HCOOH**	**0.5 M $KHCO_3$**	**−0.77 vs. RHE**	**100 %**	**24 h**	[101]
Sn–N_6-MOFs	**HCOOH**	**0.5 M $KHCO_3$**	**−1.23 V vs. RHE**	**85 %**	**6 h**	[86]
Sn-MOF	**HCOOH**	**0.5 M $KHCO_3$**	**−1.2 V vs. RHE**	**80 %**	**35 h**	[87]
N, O-coordinated Zn-MOFs	**HCOOH**	**0.5 M $KHCO_3$**	**−1.57 V vs. RHE**	**90.2 %**	**5 h**	[102]

Writing – original draft, Supervision, Formal analysis, Data curation. **Arumugam Thangamani:** Data curation. **Saravanan Rajendran:** Data curation. **A. Jalil:** Data curation. **Pramod K. Kalambate:** Supervision. **Devaraj Manoj:** Supervision. **Shiao-Wei Kuo:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The data that has been used is confidential.

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