Nanostructured nonprecious metal catalysts for electrochemical reduction of carbon dioxide

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Abstract

Electrochemical reduction of carbon dioxide powered by renewable electricity represents a promising solution for energy and environmental sustainability. To enable this technology, active and selective catalysts must be developed. Noble metals exhibit excellent activity but are hampered by their low abundance and high cost. Thus, searching for efficient nonprecious metal catalysts for practical applications is vital. In this review, the recent progress on nanostructured nonprecious metal catalysts for electrochemical reduction of carbon dioxide is summarized. These catalysts are classified into five categories: metals, partially oxidized metals, metal oxides and sulfides, doped carbons, and organic frameworks. The areas of focus are material synthesis, structure and components, catalytic performance, and reaction mechanisms. Several important factors that affect activity, such as particle size, interface strain, grain boundary, crystal facet, oxidation state, heteroatom configuration, and organic hybrid, are discussed. Finally, some perspectives are provided for future developments and directions of the synthesis and functionalization of nonprecious metal catalysts, with emphasis on the potential advantages of nanoporous materials for carbon dioxide reduction.

Key words: Carbon dioxide, electrochemical reduction, energy conversion, nonprecious metals, nanostructures

1. Introduction

To satisfy the energy demand of an increasing world population, fossil fuels including coal, petroleum, and natural gas are being burned on an unprecedented scale. Unfortunately, this leads to the annual release of more than 30 billion tons of carbon dioxide (CO_2) into the environment, with continuous accumulation over time [1]. From a pre-industrial level of about 270 ppm, the concentration of CO_2 in the atmosphere has now surpassed the 400 ppm mark. As is well known, CO_2 is a notorious greenhouse gas that traps the sun's heat and is one of the main contributors to presently observed climate change phenomena. Therefore, reducing CO_2 production and converting CO_2 into valuable materials are urgent needs for the sustainable development of human society [2–5].

In recent years, catalytic CO_2 reduction to fuels has been investigated actively using thermochemical, photochemical, and electrochemical approaches [6–10]. Among them, electrochemical CO_2 reduction has become attractive because it has several characteristic advantages over other approaches. Specifically, the reaction can be conducted under ambient conditions, the reaction rate can be controlled easily by tuning the external bias, and the supporting electrolytes can be fully recycled so that the overall chemical consumption can be minimized to only water [11]. Moreover, an artificial photosynthesis process might be achieved if the electricity for CO_2 electrochemical reduction is derived from renewable energy, such as wind, solar, and tidal power [12]. With renewable electricity as an input, carbon dioxide and water could be converted into fuels and industrial chemicals (Fig. 1a). Such a process provides an efficient means to storage intermittent energy. However, CO_2 is very stable under environmental conditions, and a highly negative potential is needed to drive the reduction reaction. Meanwhile, there are several proton-assisted multiple-electron-transfer processes with similar potential, which makes it difficult to control the selectivity. For example, the reduction reactions can occur via 2-, 6-, 8-, and 12-electron transfer processes (Fig. 1b) and result in a variety of products, including carbon monoxide (CO), formic acid (HCOOH), methanol (CH_3OH), formaldehyde (HCHO), methane (CH_4), ethylene (CH_2CH_2), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), acetate (CH_3COOH), and many others [13]. Moreover, the hydrogen evolution reaction (HER) usually prevails over CO_2 reduction in aqueous electrolytes. Therefore, active electrocatalysts need to be developed that promote the CO_2 reduction reaction with high efficiency and selectivity while suppress the competing HER.

Nanostructured metal catalysts have attracted much attention for electrochemical CO₂ reduction due to their unique properties compared to their polycrystalline counterparts. They have a high catalytic surface area and contain a large portion of edge or low-coordinated sites, which have different catalytic behaviors as compared to fully coordinated sites on the flat surface of their bulk samples. The improved catalytic performances are demonstrated in nanostructured catalysts. Typically, nanostructured noble metals such as Au, Ag, and Pd have exhibited highly selective conversion of CO₂ to CO at relatively low overpotentials [14–26]. For example, monodisperse 8-nm Au nanoparticles showed a faradaic efficiency (FE) of up to 90% at -0.67 V vs. the reversible hydrogen electrode (RHE) in an aqueous 0.5 M KHCO₃ electrolyte [16]. Density functional theory (DFT) calculations suggested that edge sites on the Au nanoparticle surface favored CO evolution, while corner sites favored HER. Interestingly, based on this result, ultrathin Au nanowires with dominant edge sites on their surface were prepared and demonstrated to be significantly more active and selective than nanoparticles [18]. At -0.35 V vs. RHE, the FE reached 94% for CO production and stayed at this level for 6 h without any noticeable change. Similarly, nanostructured Ag and Pd have also shown excellent activity to selectively convert CO₂ to CO [27–38]. Nanoporous Ag exhibited an approximately 92% selectivity for CO at a mediocre potential of -0.6 V vs. RHE [35], while on 2.4- and 3.7-nm Pd, the maximum FE value of 91.2% was reached at -0.89 V vs. RHE [38]. However, precious metals are hampered by their low abundance and high cost, which restrict their practical and large-scale application. Thus, searching for abundant and efficient electrocatalysts with selectivity toward valuable fuels is vital for commercializing CO₂ electroreduction technologies.

Although several review articles related to CO₂ reduction have been published, nonprecious metal catalysts have not been systematically discussed [39–45]. Less expensive and environmentally friendly materials such as Cu, Zn, Sn, Bi, Co, carbons, and organic frameworks have demonstrated promise for the reduction of CO₂ to hydrocarbons, formic acid, and CO. In the early study, most of their bulk metals have been used as electrocatalysts for CO₂ reduction and shown some activities [46–51]. For example, high purity polycrystalline Cu produced CH₄ and C₂H₄ with FE of 33.3 % and 25.5 %, respectively, at -1.44 V vs. the standard hydrogen electrode (SHE) with the current density of 5 mA cm⁻² and *in-situ* electrodeposited Cu electrode improved the selectivity by changing the surface morphology with the overall FE of 79% [49].

Bulk Zn metal showed high selectivity for CO with FE of 79.4% at -1.54 V *vs.* SHE while bulk Sn metal showed excellent selectivity for HCOOH with FE of 88.4% at -1.48 V *vs.* SHE. Although bulk metals exhibited interesting performance, it was found they were easily poisoned by impurities due to their low surface area. Furthermore, the early results mainly reported the selectivity of metals, but the energy efficiency (*e.g.*, overpotential), activity stability, material synthesis, and structure characterization have been very little reported. By combining with the modern methods and technologies, the CO₂ electrocatalyst development exhibited several new trends in the recent research. Typically, nanotechnologies are well applied in the fabrication of nonprecious metal catalysts, and nanostructured metals, partially oxidized metals, and metal compounds exhibit better activities than their bulk samples. The material structure and catalytic properties are studied in depth by newly developed analysis and characterization technologies. More importantly, the novel non-metal or little-metal doped carbons and organic frameworks have also shown outstanding performance for CO₂ reduction, comparable to noble metals, which may represent a future research direction. Therefore, a comprehensive review specifically focused on nonprecious metal catalysts is necessary to promote the practical applications of CO₂ conversion technology.

In this article, the synthesis of specific nanostructures, their unique catalytic properties, and their reaction mechanisms for nonprecious metal catalysts are systematically summarized. These catalysts are classified into five categories: metals, partially oxidized metals, metal oxides and sulfides, doped carbons, and organic frameworks. The important factors that affect activity are discussed. Future strategies are proposed for the design of highly selective and efficient CO₂ reduction electrocatalysts.

2. Metal catalysts (Cu and Zn)

Cu has been known as an unique metal catalyst in its ability to produce a high quantity of hydrocarbon fuels from the electrochemical reduction of CO₂ since the first report by Hori *et al.* in 1985 [52–55]. A total of 16 different CO₂ reduction products have been observed on Cu foil using a highly sensitive electrochemical cell combined with gas chromatography and nuclear magnetic resonance spectroscopy [56]. Among them, the hydrocarbons of methane and ethylene products have the largest current efficiencies, while the remaining 14 products are oxygenates, 11 of which are C₂ and C₃ products. By comparing the activity of different transition metals, it is found that the product yield and composition of the CO₂ reduction depend on the transition metal's binding energy of CO, which is believed to be an important intermediate in the reduction process. Interestingly, Cu possesses an intermediate binding energy for CO, which may be the reason for its ability to catalyze the formation of more reduced products. However, Cu has three drawbacks as a CO₂ reduction electrocatalyst: large overpotentials, poor selectivity, and instability for a long time. In order to enhance the performance of Cu electrodes, various kinds of nanostructured Cu catalysts have been prepared, including zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanowires, two-dimensional (2D) overlayers, and three-dimensional (3D) foams, and their influence factors on activity have been explored, such as size effect, density effect, strain effect, grain-boundary effect, and crystal-facet effect.

The size effect has been regularly utilized to tune the catalytic activity and selectivity of 0D metal nanoparticles [57–60]. Reske *et al.* examined the catalytic behavior of Cu nanoparticles with different particle sizes that ranged from 2 to 15 nm [57]. Compared to a bulk Cu electrode, the catalytic activity and selectivity for H₂ and CO dramatically increased with decreasing Cu particle size, particularly for particles below 5 nm, while hydrocarbon (methane and ethylene) selectivity was suppressed on nanoscale Cu particles. The authors used a spherical Cu particle model to rationalize the experimental results and found that the population of low-coordinated surface sites changed significantly with the particle size. As shown in Fig. 2, below 2 nm, a drastic increase in undercoordinated atoms with CN < 8 is observed. These strongly binding sites simultaneously accelerated HER and CO₂ reduction to CO. In contrast, Baturina *et al.* found that carbon-supported Cu nanoparticles were more active toward C₂H₄ generation than electrodeposited smooth copper films [59]. By comparing the activities and selectivities of 10- to 30-nm supported Cu

nanoparticles, a higher ratio of C_2H_4/CH_4 was observed in smaller Cu nanoparticles with a size of 12 nm. In another experiment, a 50- to 100-nm Cu-nanoparticle-covered electrode also showed better selectivity toward hydrocarbons compared with the electropolished and argon-sputtered Cu electrode [60]. These data illustrate that it is crucial to control the sizes of Cu nanoparticles and that too-small sizes will decrease the selectivity for CO_2 reduction.

In addition to particle sizes, the interparticle distance (particle density) in a prepared electrode plays an important role in the activity and selectivity of Cu catalysts. Manthiram et al. found that the level of copper catalyst loading on the glassy carbon support had an enormous impact on the selectivity for methane [61]. Dispersible copper nanoparticles supported on glassy carbon (n-Cu/C) achieved up to 4 times greater methanation current densities, with an average FE of 80%, compared to copper foil electrodes. By fabricating evaporated Cu electrodes, it was observed that the FE and current density of CH_4 were inversely proportional to film thickness, and thinner films exhibited higher performances. It is noted that the authors observed an interesting morphological evolution phenomenon, as shown in Fig. 3. The small particles (~7 nm) grew into big particles (~24 nm) during the course of the electrochemical CO_2 reduction. Moreover, irrespective of the initial size of the nanoparticles on glassy carbon, the sizes of evolved particles are always ~25 nm in diameter, even if larger particles are used. The morphological evolution may be due to a combination of particle coalescence and dissolution–redeposition, however, which points out an important problem about the size stability of nanoparticles during electrochemical reduction. The authors also put forward a possible methanation mechanism from the Tafel slope (Fig. 3e). The reaction process first involves a 1-electron-transfer pre-equilibrium step to form an adsorbed radical, and then the second CO_2 molecule reacts with the adsorbed CO_2 radical, which is the rate-limiting nonelectrochemical step.

To control the product selectivity of CO_2 reduction, 2D nanoscale thin Cu layers deposited on foreign metal substrates have been investigated [62–66]. The catalytic behaviors of such nanolayers can be drastically changed due to the effects of the lattice strain and layer-substrate electron interaction [45]. Reske et al. investigated the performance of Cu overlayers with different thicknesses ranging from 1 monolayer to 15 nm supported on a polycrystalline Pt substrate [62]. As shown in Fig. 4, the ratio of CH_4/C_2H_4 could be controlled with the Cu layer thickness and the reduction potential. The 1-monolayer Cu showed an almost

constant ratio over the potential range from -0.8 V to -1.1 V vs. RHE, with a better selectivity for C₂H₄ than thicker Cu layers. In another, similar study, Varela et al. chose Cu overlayers on Pt(111) and Pt(211) surfaces to investigate the strain effect [63]. They found that the selectivity toward hydrocarbons on the copper overlayers was much lower than on polycrystalline copper due to a higher selectivity for hydrogen evolution. By using in situ electrochemical scanning tunneling microscopy (EC-STM), it was observed that the Cu overlayer changed from a flat to a granular structure in the presence of CO, exposing part of the Pt surface and providing active hydrogen evolution sites. The restructuring of Cu deposits was also observed on a Cu-modified Pt single electrode [64]. This is consistent with the morphology evolution of Cu nanoparticles on glass carbon, which may be involved in the chemical etching of Cu and its electrochemical redeposition. In contrast, by using in situ high-energy-resolution fluorescence-detection X-ray absorption spectroscopy (HERFD XAS), Friebe et al. demonstrated that a Cu monolayer deposited on an Au(111) single crystal exhibited better stability against oxidation than Cu multilayers on the same substrate at low potentials (< 0.5 V vs. RHE), while at high potentials (> 0.5 V vs. RHE), it directly converted to CuO rather than forming an intermediate Cu₂O phase [65]. The large lattice mismatch of 12.5% between Cu and Au was expected to influence the binding energy of intermediates. However, the alloying of Cu with the Au substrate was observed for Cu overlayers, which would affect the stability of this strained bimetallic catalyst. Thus, substrate selection is very important for the activity of Cu nanolayer catalysts.

With the progress in nanofabrication technologies, complicated nanostructured Cu catalysts with 3D morphologies have been prepared for CO₂ reduction [66–77]. Zero-dimensional nanoparticles, 1D nanowires or nanorods, or 2D nanosheets are assembled into 3D hierarchical structures, which greatly increase specific areas with more exposed active sites and improve the capability of mass transfer. Recently, Li et al. prepared oxide-derived Cu (OD-Cu) catalysts by annealing Cu foil in air and electrochemically reducing the resulting Cu₂O layers [67]. Thick Cu₂O layers (~3 μm) with a dense array of nanorods were formed by annealing at 500°C for 12 h. After in situ electroreduction, the rod morphology was intact, but smaller particles (~20 nm) were embedded within the rods. The OD-Cu exhibited a high efficiency for CO₂ reduction, with a peak FE of ~45% for CO production at potentials of -0.3 to -0.5 V vs. RHE, and a peak FE of 33% for HCOOH production at potentials of -0.45 to -0.65 V vs. RHE (Fig. 5). Moreover, the activity of

the modified electrodes was stable over the course of several hours. Later, OD-Cu was used for CO electroreduction and produced multi-carbon oxygenates (ethanol, acetate, and n-propanol) with up to 57% FE at modest potentials of -0.25 to -0.5 V vs. RHE [68]. By comparing OD-Cu to commercial Cu nanoparticles, the authors proposed that the CO reduction activity was not a consequence of nanocrystallite size or morphology but of grain boundaries participating in the catalysis. Temperature-programmed desorption of CO on low-temperature (130 °C) H₂ reduced OD-Cu revealed the presence of surface sites with strong CO binding that are distinct from the terraces and stepped sites found on polycrystalline Cu foil [69]. However, after annealing at 350 °C, the activity for CO reduction was 44-fold decreased and the Faradaic efficiency was less than 5%, accompanying by a reduction in the proportion of strong CO binding sites. This indicates that such strong CO binding sites are supported by grain boundaries and may be the active sites for CO reduction. Since the success of Cu₂O-derived Cu, CuO-derived 3D Cu nanowire arrays have been prepared and exhibited excellent selectivity for CO, with a maximum FE of 60%, higher than that for polycrystalline Cu [70, 71]. A CuO-derived Cu nanoflower was also reported and exhibited an FE of 40% for HCOOH at a high overpotential. The deposition of amorphous carbon on the electrodes after catalysis was directly observed in this study [75]. Except for oxide-derived Cu, 3D Cu nanostructures can be prepared by electrodeposition of Cu⁰. Three-dimensional Cu nanofoams with a hierarchical porous structure have been synthesized using this method [76]. It was found that increasing the thickness of the copper nanofoams could enhance the FE of HCOOH up to 29%, compared to only 3% on smooth copper foil. The above results indicate that different preparation conditions can yield different surface structures and morphologies, which then exhibit different catalytic activities, stability, and selectivity. Therefore, a rational design and synthesis of 3D Cu nanostructures will induce the efficient active sites for CO₂ reduction.

The effect of Cu crystal facets on selectivity for CO₂ reduction has been investigated by experiments and theoretical calculations. Hori et al. reported that single-crystal Cu(100) favorably yielded C₂H₄, while Cu(111) mainly gave CH₄ from CO₂ [78]. Interestingly, when high-index facets such as Cu(711) and Cu(911) were introduced, they significantly promoted C₂H₄ formation and suppressed CH₄ formation, with a C₂H₄/CH₄ ratio value of 14, 2 orders of magnitude higher than that for Cu(111). The enhancement may be due to the increased population of atomic steps exposed on such high-index facets. Hori's observations were

later confirmed by Koper and co-workers using online electrochemical mass spectrometry [79–81]. They compared Cu(111) and Cu(100) single-crystal electrodes and observed two different reaction mechanisms for hydrocarbon formation in the CO reduction: one pathway had a common intermediate with the formation of CH₄ on both facets and took place preferentially on Cu(111) facets or steps; in the second pathway, CO was selectively reduced to C₂H₄ on the Cu(100) facet through the formation of a surface-adsorbed CO dimer.

Mesocrystals represent a new class of nanostructured solids made from crystallographically oriented nanoparticles. Recently, Chen et al. prepared a Cu mesocrystal by in situ electrochemical reduction of a thin CuCl film [82]. At -0.99 V vs. RHE, a C₂H₄/CH₄ FE ratio of ~18 was achieved in an aqueous 0.1M KHCO₃ electrolyte. High-resolution transmission electron microscopy (HRTEM) revealed the presence of both Cu(100) facets and atomic steps in the Cu mesocrystals, which were assigned as active sites for the production of C₂H₄. The reaction mechanisms on different crystal facets have been investigated by DFT calculations. Peterson et al. proposed that the protonation of the adsorbed CO to CHO* was the potential determining step of methane formation on open facets of Cu(211) and Cu(100) [83, 84]. However, on the Cu(111) facet, the initial protonation of CO₂ was predicted to dictate the potential requirements. Fig. 6d shows the *d*-orbital density of states for each crystal orientation. The distribution of states shifts toward the higher energy region from (111) to (211). The *d*-band center changes by approximately 0.2 eV between both surfaces, which is consistent with the observed variations of the adsorption energies of reactant species (Fig. 6e) [85]. Tang et al. also suggested stronger chemisorption of the CO intermediate and CHO intermediates on Cu(211) stepped surfaces as compared to the Cu(100) or Cu(111) facets [60]. Vollmer et al. experimentally verified that CO binds more strongly on Cu stepped and kinked facets such as Cu(211), Cu(221), and Cu(532) than on low-index facets by temperature-programmed desorption (TPD) of CO [86]. However, Nie et al. proposed that on Cu(111), methane and ethylene were formed via a common hydroxyl-methylidyne intermediate, *C-OH, which was subsequently hydrogenated to a common CH₂* intermediate [87]. A nonelectrochemical dimerization and C-C bond formation may occur to produce ethylene or else hydrogenate further to methane. In another interesting study, based on first-principles calculations, Chen et al. predicted that pentatwinned Cu nanowires were superior to conventional Cu catalysts for CO₂ electroreduction [88]. The pentatwinned Cu nanowires can withstand extremely high

elastic strains, and the catalytic activity on the Cu(001) facets of the Cu nanowires exceeds that on the bulk (211) surface with 2.7% tension strain. Therefore, the surface orientations of the Cu crystal have a dramatic influence on catalytic activity and product selectivity during CO₂ reduction.

Alloying is another efficient approach to enhance the catalytic activity and selectivity for CO₂ reduction. By alloying, the binding strength of intermediates on a catalyst surface can be tuned by varying the composition and ratio of metal elements [89–91]. For example, Kim et al. synthesized Au-Cu bimetallic nanoparticle alloys with different Au/Cu ratios and found that Au₃Cu nanoparticle monolayers had the highest mass activity for CO production, outperforming conventional CO₂ reduction catalysts [20]. This activity was explained in terms of the electronic effect and the geometric effect in the Au-Cu alloy, both of which synergistically optimize the binding strength of intermediates. Similar composition-dependent product selectivity of Au-Cu alloys was also observed by Christophe et al. [92]. The dilution of the copper sites at the surface readily prevented the formation of gaseous hydrogenated species and activated the production of CO. Among all the investigated compositions, the Au₅₀Cu₅₀ alloy gave the best results. In another study, Jia et al. observed that a Cu_{63.9}Au_{36.1} nanoporous film exhibited high selectivity of alcohols (methanol and ethanol) [93]. In addition to the Cu-Au alloy, Cu-Pt alloys have been investigated for CO₂ reduction [94, 95]. Guo et al. demonstrated that Cu-Pt (3:1) nanocrystals exhibited high activity and FE for CH₄ production [94]. Although some progress with Cu–noble metal alloys has been achieved, the catalytic performance still needs to be improved. Recently, Rasul et al. reported a non-noble metal electrocatalyst based on a Cu-In alloy that selectively converts CO₂ to CO with an FE of 90% at -0.6 V vs. RHE in an aqueous 0.1M KHCO₃ electrolyte (Fig. 7) [96]. The Cu-In alloy was prepared by electrochemical deposition of In on rough Cu surfaces. DFT calculations showed that the adsorption properties of Cu were perturbed by the presence of neighboring In atoms, which preferentially located on the edge sites rather than on the corner or flat sites. The excellent selectivity and stability of this non-noble metal alloy provide guidelines for obtaining efficient and low-cost electrocatalysts for CO₂ reduction in the future.

Among the metal catalysts, Zn is also a promising material due to its cost-effectiveness and potential activity for the electrochemical reduction of CO₂. Early work by Hori and Ikeda has shown some catalytic properties of bulk metallic Zn for CO₂ reduction to CO, but its efficiency are not satisfactory, especially the

poor stability caused by oxidation and dissolution under testing conditions [97–99]. Recently, nanostructured Zn catalysts have been explored and have exhibited improved performance compared to bulk Zn. For example, Rosen et al. reported a nanostructured Zn dendrite catalyst synthesized using an electrodeposition method [100]. The dendrite layer approximately 50–100 μm thick was uniformly coated on the Zn substrate. In an aqueous bicarbonate electrolyte, the Zn dendrite catalyst exhibited remarkable properties for CO_2 reduction, an order of magnitude higher activity and around 3-fold higher FE for CO production than those of bulk Zn counterparts. The authors also investigated the stability of the Zn electrode under realistic CO_2 electrolysis conditions by using scanning electron microscopy and in situ/operando X-ray absorption spectroscopy techniques. The results showed that Zn catalysts could be structurally stable at potentials more negative than -0.7 V vs. RHE, whereas severe chemical oxidation would occur at more positive potentials. Quan et al. prepared nanoscale Zn by the electrochemical reduction of anodized zinc foil [101]. A dense layer of Zn nanoplates 1 μm long and 40 nm thick was formed on the electrode surface, and fine nanoparticles (30–50 nm) were observed on the surface of the nanoplates. By the optimum combination of a nanoscale catalyst and electrolyte anion, the activity of the Zn electrode was dramatically enhanced toward the reduction of CO_2 to CO. In aqueous NaCl solution, a maximum FE of 93% was achieved for CO on the nanoscale Zn, while the FE is only 18% for CO on the bulk Zn electrode in NaHCO_3 solution (Fig. 8). Moreover, this nanoscale Zn catalyst remained stable during long-term electrolysis. This work demonstrates the importance of the electrolyte and that only after determining the optimum combination of catalyst and electrolyte can the best performance be achieved.

3. Partially oxidized metal catalysts

Compared to the zero-valence pure metal, small metastable metal oxides on metal surfaces can also participate in the CO₂ reduction by providing chemical functionality that stabilizes the incipient negative charge on CO₂ or by mediating the electron transfer directly [102–106]. As a result, the catalytic activity for CO₂ reduction can be greatly enhanced relative to a pure metal electrode. Although the potentials required for CO₂ reduction are beyond the standard reduction potentials for these oxides, metastable metal oxides are known to persist on electrode surfaces during cathodic reactions [107–109]. Chen et al. demonstrated the importance of tin oxide (SnO_x) on the Sn surface for CO₂ reduction by comparing the activity of Sn electrodes with different pre-electrolysis treatments [110]. Two pieces of high-purity Sn foil were used. The untreated Sn foil electrode with a native SnO_x layer exhibited potential-dependent CO₂ reduction activity consistent with previously reported activity, while after acid etching of the oxide layer, the exposed fresh Sn⁰ surface exhibited higher overall current densities but almost exclusive H₂ evolution over all of the potentials. Subsequently, the authors prepared a thin-film catalyst by simultaneous electrodeposition of Sn⁰ and SnO_x on a Ti foil. As expected, this catalyst exhibited up to 8-fold higher partial current density and 4-fold higher FE for CO₂ reduction than the untreated Sn foil electrode. Although it remains unclear upon which site the CO₂ reduction actually occurs, namely, the interface between Sn and SnO_x or only on the SnO_x surface, the importance of SnO_x for CO₂ reduction is undeniable.

The role of the surface oxide thickness on the activity of Sn nanoparticles for CO₂ reduction was further investigated by Wu et al. using a full electrochemical cell [111]. They found that the initial SnO_x thickness strongly affected selectivity toward the formation of CO and formate. The 100-nm Sn nanoparticles with a native 3.5-nm SnO_x layer exhibited the highest FE (64%) toward formate formation, while the maximum FE (35%) toward CO production was observed in the Sn nanoparticles possessing an oxide thickness of 7.0 nm, formed by annealing the Sn nanoparticles at 180°C for 6 h. However, further increasing the thickness of the SnO_x layer led to the enhancement of hydrogen evolution. The importance of the oxide layer on the Sn electrode was also evaluated by Zhang et al. [112]. They found that if the etched Sn plate electrode was exposed in the air for over 24 h, its catalytic performance for CO₂ reduction would be restored to an FE similar to that of untreated Sn plate, but the electrolysis current density for this electrode was around

1.5-fold higher than that for an untreated Sn electrode. The etching treatment made the electrode surface rough and enlarged the active area, which accelerated the reaction rate. Won et al. demonstrated that the CO₂ conversion selectivity on SnO_x/Sn electrodes was correlated to the native oxygen content [113]. They found that the FE for formate was proportional to the initial O content in the surface SnO_x layer. The abundant O species that survived under highly reductive conditions effectively stabilized the intermediate CO₂^{•-} species, thus facilitating formate production. Based on this understanding, the authors prepared a hierarchical Sn dendrite electrode with high oxygen content, consisting of a multi-branched conifer-like structure (Fig. 9a–c). This electrode exhibited superior capability for formate production (228.6 μmol h⁻¹ cm⁻² at -1.36 V vs. RHE) as well as stable operation over 18 h. The above results clearly indicate that the surface oxide of the Sn catalysts is essential for CO₂ reduction. Later, Zhang directly synthesized SnO_x nanocrystals by a facile hydrothermal method for CO₂ reduction to formate [114]. A particle-size effect was observed on Sn catalysts, and the maximum current efficiency occurred on 5-nm SnO_x nanoparticles. This work also demonstrated the importance of the support type. For instance, a higher FE (93.6%) for formate production was obtained with a reduced nano-SnO₂/graphene, nearly twice the current density (10.2 mA cm⁻²) as for SnO₂/carbon black. The strong electron-donating ability of graphene as compared to carbon black was reflected by the negative shift in binding energies in the Sn3d XPS spectra. Although the authors claimed that most of the SnO₂ was reduced to Sn⁰ during the CO₂ reduction process, the presence of a partial oxide could not be excluded.

Despite these works, the key surface species associated with CO₂ reduction at partially oxidized tin catalysts have not been identified [115–118]. Recently, Baruch et al. studied the reduction of CO₂ on a mixed SnO_x/Sn film cathode by using in situ attenuated total reflectance infrared spectroscopy (ATR-IR) [119]. They directly observed a surface carbonate species that was present at the Sn catalyst specifically when CO₂ reduction took place. Analysis of the potential and time-dependent IR data indicated that a surface-bound tin-carbonate species was an active intermediate in the reduction process. To determine the oxidation state of the catalytically active sites, the authors compared the catalytic behavior of the Sn^{II}₆O₄(OH)₄ and Sn^{IV}O₂ nanoparticles and found that they showed very little difference in the product distributions over a variety of potentials, which suggested that the catalytic species may be the Sn^{II}

oxyhydroxide surface. Based on these experiments, a mechanism governing the reduction of CO₂ on tin electrodes was proposed, as shown in Fig. 9d. The same group also demonstrated a similar behavior on partially oxidized indium cathodes [120]. On an anodized In/In₂O₃ electrode, the formate production involved the insertion of CO₂ at the indium interface to form an electroactive surface bicarbonate species.

Except for Sn, partially oxidized Bi/Bi³⁺ materials have shown excellent CO-selective capabilities in ionic liquid [121–124]. Recently, the Rosenthal group synthesized a rosebud-type Bi thin film on a glassy carbon electrode (GCE) by electrochemical deposition (Fig. 10) [121]. The high-resolution XPS spectra of Bi 4f_{7/2} revealed that the ratio of Bi⁰ to Bi³⁺ was ~2:1. The oxygen and halide atoms contained in the electrolyte were incorporated into the electrodeposited material to balance the charge of the Bi³⁺ ions. A current density of ~4 mA cm⁻² was achieved with a CO efficiency of 95% at -1.95 V vs. SCE in the acetonitrile containing a 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) electrolyte. Later, the same group optimized the type and concentration of the ionic liquid promoter. In the 300-mM 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) catholyte solution, high current densities of $j_{\text{CO}} = 25\text{--}30 \text{ mA cm}^{-2}$ were achieved with the energy efficiencies of $\Phi_{\text{CO}} \approx 80\%$ [122]. Moreover, an in situ electrodeposition pathway was developed for the Bi catalyst by using a soluble Bi³⁺ precursor in the CO₂-saturated catholyte solution, which significantly streamlines the preparation of electrode assemblies for CO production [123]. This in situ formation strategy was also extended to Sn, Pb, and Sb catalysts. Among them, the electrochemically prepared Sn catalysts proved to be highly active, selective, and robust platforms for CO evolution.

Recently, in addition to the above conventional catalysts, novel partially oxidized atomic Co layers were reported by Gao et al. to show outstanding performance for CO₂ reduction [125]. To evaluate the role of the two different catalytic sites, the authors fabricated freestanding 4-atom-thick Co sheets with and without surface Co oxide using a ligand-confined growth strategy in which dimethylformamide and *n*-butylamine were used for reducing the metal ions and enforcing a sheet-like morphology, respectively. Controlled fabrication of either partially oxidized or pure Co atomic layers was achieved by varying the reaction times. HRTEM images revealed the presence of a cubic Co₃O₄ domain, which was embedded in the metallic Co lattice (Fig. 11). As an electrocatalyst for CO₂ reduction, it was found that cobalt mainly produces HCOOH, and 4-atom-thick Co nanolayers had higher intrinsic activity and selectivity toward HCOOH with lower

overpotentials than bulk Co samples. Interestingly, partial oxidation of the atomic layers significantly increased their intrinsic activity and generated a current density of 10.59 mA cm^{-2} at -0.85 V vs. SCE in an aqueous $0.1 \text{ M Na}_2\text{SO}_4$ electrolyte, which was about 10 times larger than that of pure 4-atom-thick Co. Moreover, this catalyst remained stable in a 40-h electrocatalysis test with approximately 90% selectivity at an overpotential of only 0.24 V . This work strongly demonstrates that the correct morphology and oxidation state can transform a nearly noncatalytic material for CO_2 reduction into an active catalyst, which provides new opportunities for manipulating and improving the performance of nanostructured catalysts.

4. Metal oxide and sulfide catalysts

In addition to partially oxidized metal catalysts, metal oxides with high valences of metal ions also show great promise for CO₂ reduction. For example, a nanostructured TiO₂ film could catalyze CO₂ electroreduction by the reversible Ti³⁺ to Ti⁴⁺ transformation [126]. Ti³⁺ species were formed when the TiO₂ film was subjected to negative potentials, which were identified as active reduction sites. The initial 1-electron reduction process occurred by the binding of CO₂ to catalytically active Ti³⁺ with the electron transfer. Another interesting example is Ga₂O₃. Sekimoto et al. reported on the high-selectivity electrochemical reduction of CO₂ to HCOOH with an FE of over 80% using conductive single-crystal Sn- or Si-doped Ga₂O₃ [127]. DFT calculations demonstrated the existence of a stable intermediate state (H-CO₂) on the surface of the Ga₂O₃. Recently, Gao et al. synthesized 1.72- and 3.51-nm Co₃O₄ layers through fast-heating the respective precursors of ultrathin Co(CO₃)_{0.5}(OH)·0.11H₂O layers [128]. Comparison of the electrochemically active surface area and the CO₂ adsorption isotherms demonstrated that the ultrathin Co₃O₄ layers had many more active sites and could adsorb higher amounts of CO₂ as compared with the bulk samples. DFT calculations revealed that the charge density around the conduction band edge in the ultrathin Co₃O₄ layer was increased noticeably and was more dispersive than in the bulk Co₃O₄. These changes would be beneficial for faster carrier transport to participate the CO₂ reduction reactions along the 2D conducting channels. As a result, the 1.72-nm-thick Co₃O₄ layers had over 1.5 and 20 times higher current density than that of the 3.51-nm-thick Co₃O₄ layers and the bulk counterpart, respectively.

MoO₂ microparticles also showed high activity for electrochemical CO₂ reduction in organic solvents such as acetonitrile and dimethylformamide. Oh et al. found that the onset overpotential of MoO₂ for CO₂ reduction was below 0.2 V in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) [129]. The activity was much higher at -20°C than at room temperature, and this activity was further promoted by a small amount of water. Later, the same authors investigated the effect of ionic liquids on the MoO₂ catalyst [130]. Similarly to the Bi-based catalyst, the addition of BMIM-PF₆ in acetonitrile significantly enhanced the activity of MoO₂ for CO₂ reduction with an overpotential as low as 0.04 V. The results suggested that ionic liquids act as both electrolytes and co-catalysts, which not only decreased overpotentials but also increased product selectivity.

Recently, MoS₂ and related layered materials have attracted significant attention due to their low price and prominent catalytic features. Chan et al. predicted theoretically by DFT calculations that the edge sites of crystalline MoS₂ could be the catalytic sites for CO₂ reduction [131]. They proposed a new way of lowering the overpotential for CO₂ reduction: designing catalysts that selectively bind key reaction intermediates to different sites. Their analysis of the active edges of MoS₂ demonstrated that the bridging S atoms selectively bind CHO and COOH, and metal atoms selectively bind CO. The resultant deviation from the transition-metal scaling relationship of intermediates greatly improved activities over the best transition-metal catalysts. Interestingly, Asadi et al. demonstrated experimentally that layer-stacked bulk MoS₂ with Mo-terminated edges showed superior CO₂ reduction performance with a high current density and low overpotential (0.054 V) in an ionic liquid solution [132]. The reduction current density reached a maximum of 65 mA cm⁻² at -0.764 V vs. RHE with 98% FE for CO in a solution of 4 mol% EMIM-BF₄ and 96 mol% water (Fig. 12). The first principle modeling revealed that the Mo-terminated edges of MoS₂ possessed a high d-electron density, similar to a metallic character. Meanwhile, the presence of EMIM⁺ cations around CO₂ molecules reduced the reaction barrier for electrons passing into CO₂. Thus, the observed highly catalytic performance is attributed to a synergistic action of the MoS₂ catalyst and the EMIM-BF₄ ionic liquid. In another work, Li et al. synthesized amorphous molybdenum sulphide on a polyethylenimine (PEI)-modified reduced graphene oxide substrate for CO₂ reduction in an aqueous NaHCO₃ medium [133]. Instead of ionic liquid, here PEI played crucial roles, suppressing HER and stabilizing the intermediate species in the CO₂ reduction process. The composite catalyst could produce CO at overpotentials as low as 0.14 V and reach a maximum FE of 85.1% at an overpotential of 0.54 V. However, the current density is obviously inferior to that of ionic liquid-containing systems. This suggests that the introduction of a small co-catalyst may be necessary to enhance the reaction kinetics.

5. Doped carbon catalysts

Doped carbons have shown a high catalytic performance comparable to that of noble metal catalysts (e.g., Pt) for an oxygen reduction reaction (ORR) [134–138]. The insertion of heteroatoms such as N, S, P, and B in the carbon lattice converts the neutral carbon atoms into positively or negatively charged atoms, which become active sites. Recently, N-doped carbons have demonstrated superior catalytic activity for CO₂ reduction. Kumar et al. synthesized carbon nanofiber (CNF) catalysts by the pyrolysis of electrospun nanofiber mats of heteroatomic polyacrylonitrile (PAN) polymer for CO₂ reduction [139]. In an aqueous EMIM-BF₄ solution (25 mol% EMIM-BF₄ and 75 mol% water), the carbon nanofiber catalyst exhibited low overpotential (0.17 V) and more than an order of magnitude higher current density compared with the silver catalyst under similar experimental conditions. A maximum FE of 98% for CO formation was observed at -0.573 V vs. SHE. After detailed analysis of the change in N XPS spectra before and after electrolysis, the authors attributed the catalytic proficiency of CNFs to the highly positive charged carbon atoms. Similarly, N-doped carbon nanotube (NCNT) arrays were demonstrated for the high-efficiency electrochemical reduction of CO₂ by Wu et al. [140, 141]. The NCNTs were synthesized by the liquid chemical vapor deposition (CVD) method, and the N-bonding configuration and content were tuned by using different precursors and various growth temperatures (Fig. 13). In contrast with the last work, this work showed that the catalytic activity of NCNTs depended on the structural nature of doped N in NCNTs and the defect density. The presence of graphitic and pyridinic N defects significantly decreased the overpotential (~-0.18 V) and increased the selectivity toward CO formation (~80%) in comparison to pristine CNTs. **DFT calculations predict the lowest absolute overpotential of 0.20 V for COOH* at a pyridinic N site. Excess negative charge in the graphite basal plane is localized at the nitrogen atoms in the pyridine-like structure, resulting in its higher catalytic activity. The electronic density of states show that pyridinic defects retain a lone pair of electrons, which can bind CO₂, while for graphitic-like nitrogen, electrons are located in the p* antibonding orbital, making them less accessible for CO₂ binding.** The same authors further prepared N-doped 3D graphene foam and observed the dependence of catalytic activity on pyridinic N [142]. Another interesting work, Chai et al. showed that the interplay of N-doping and curvature could effectively tune the

activity and selectivity of graphene/CNT catalysts by DFT and ab initio molecular dynamic calculations [143]. They found that for the graphitic N doped zigzag edge graphene, an electron was donated from graphitic N to the unoccupied electronic states of near edge C just above the Fermi level, which doubles its occupied electronic states just below the Fermi level and shifts those closer to the Fermi level. The increased occupied electronic states just below the Fermi level of the edge C readily facilitate electron transfer to a CO₂ molecule, that is to say, the C sites that possess high electronic density of states are the most likely active sites. Moreover, the selectivity can be changed by the curvature effect. The graphene catalyst without curvature showed strong selectivity for CO/HCOOH production, whereas the CNT with a high degree of curvature is effective for both CH₃OH and HCHO production. Thus, it is inconsistent with regard to the active sites of N-doped carbons, and further work is needed to elucidate this matter.

In order to improve the performance of N-doped carbons, Zhang et al. applied an ammonia plasma treatment on carbon surfaces for N-doping followed by the adsorption of PEI [144]. As a co-catalyst, the PEI overlayer could stabilize the reduced intermediate CO₂^{•-} and concentrate CO₂ molecules. The combination of N-doping and PEI synergistically enhanced the activity. In an aqueous 0.1 M KHCO₃ electrolyte, a maximum FE of 87% for HCOOH production was reached with a current density of 9.5 mA cm⁻² at -1.8 V vs. SCE on the 3D graphenated carbon nanotube (GCNT)/PEI composite catalyst (Fig. 14). Except for the introduction of a co-catalyst, metal and N co-doping in carbon (M-N-C) has been explored as an efficient catalyst for CO₂ reduction by Varela et al. [145]. Commercial carbon blacks were functionalized with N and Fe or Mn ions using pyrolysis and acid leaching, which may produce M-N-C complexes. The resulting M-N-C catalysts were found to be active and highly CO selective electrocatalysts outperforming bulk Au. Interestingly, according to CO selectivity and methane formation trends combined with CO adsorption studies, the authors proposed that nitrogen moieties were active sites for CO production, while the metal centers acted as active sites for hydrocarbon formation. Although this result is consistent with model calculations by Rossmeisl and co-workers [146], the detailed mechanism is still unclear.

Another kind of unique carbon catalyst for CO₂ reduction is doped diamonds, which have a wide potential window, low background capacitive current, and very high stability. Nakata et al. investigated the boron-doped diamond (BDD) electrode for electrochemical reduction of CO₂ [147]. In a methanol solution

containing tetrabutylammonium perchlorate (TBAP), a maximum FE (74%) for formaldehyde was observed at -1.7 V vs. Ag/Ag⁺. Furthermore, the production of formaldehyde could be performed using seawater as a source of both electrons and protons by using this BDD catalyst. This high activity was attributed to the sp³-bonded carbon of the BDD. Later, Liu et al. prepared an N-doped nanodiamond/Si rod array (NDD/Si RA) for CO₂ reduction via a two-step synthesis strategy: the Si (resistivity of 0.001 Ω·cm) RA substrate was first fabricated by photolithography, and then, NDD film was deposited on the pretreated substrate by microwave plasma enhanced chemical vapor deposition [148]. Interestingly, in an aqueous 0.5 M NaHCO₃ electrolyte, the NDD/Si RA preferentially converted CO₂ to acetate over formate with a high FE of 91.2–91.8% at -0.8 to -1.0 V vs. RHE (Fig. 15). N-doping-induced N-sp³C species were assigned as the active sites. By in situ infrared spectrum, the authors revealed that the main pathway for CO₂ reduction might be CO₂ → CO₂^{•-} → (COO)₂[•] → CH₃COO⁻. The catalytic capability of doped diamonds shows an alternative route to convert CO₂ into rare products such as formaldehyde and acetate.

6. Covalent or metal organic frameworks (COFs or MOFs)

Organic molecular catalysts such as transition metal complexes provide opportunities for tuning activity and selectivity by systematically changing their chemical structures; specifically, their nanostructured assemblies can increase the concentration of active sites and enhance the reaction rate [149–152]. Recently, incorporating tunable molecular units within COFs and MOFs gave rise to a new kind of electrocatalyst that combines the advantageous features of both molecular and heterogeneous systems with improved activity and selectivity for CO₂ reduction. Li et al. showed that COFs comprising cobalt porphyrins were highly active, stable, and selective catalysts for electrochemical CO₂ reduction to CO in an aqueous 0.5 M KHCO₃ electrolyte [153, 154]. The porous COF structure was prepared by linking cobalt porphyrin catalysts with organic struts through imine bonds (Fig. 16). By increasing the length of the organic strut and diluting catalytic cobalt with an inactive copper unit, the pore size in COFs was enlarged, and the proportion of the active sites exposed to the reactant was increased, leading to the enhanced turnover frequency on a per-cobalt basis. This organic framework catalyst exhibited high FE (90%) and turnover numbers (up to 290,000) with an overpotential of -0.55 V, which is a 26-fold improvement in activity compared with the molecular cobalt complex. X-ray absorption spectroscopy (XAS) was used to evaluate how the surrounding COF influenced the electronic structures of incorporated catalytic cobalt porphyrin units. When a reduction potential (-0.67 V) was applied to the COF catalyst under a carbon dioxide atmosphere, the Co K-edge XAS spectra revealed a line-shape change consistent with the partial reduction of Co(II) to Co(I). This catalyst also exhibited an additional pre-edge feature not present in the cobalt porphyrin molecular, which illustrated that the COF environment could directly modulate the electronic properties of molecular centers coupled into the extended lattice. The interaction between the metal and COF lattice could furnish a cobalt center with a more delocalized electronic structure. Except for COFs, cobalt-porphyrin was also incorporated into MOFs such as Al₂(OH)₂TCPP-Co (TCPP-H₂ = 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate) by Kornienko et al. [155]. The active site, inorganic backbone, and thickness/loading were rationally chosen, and the resulting MOF was integrated onto a conductive support to form thin film. This MOF catalyst showed selectivity for CO production in excess of 76% and stability over 7 h with a per-site turnover number (TON) of 1400. In situ spectroelectrochemical measurements revealed that the Co^{II} centers are

reduced to Co^{I} throughout the MOF and subsequently reduce CO_2 . At the same time, Hod et al. incorporated Fe-porphyrin into MOF-525 for CO_2 reduction [156]. In the Fe-MOF-525 film, the high surface concentration of Fe-porphyrin was observed ($\sim 1015 \text{ sites cm}^{-2}$), which is equivalent to ~ 900 monolayers of surface-adsorbed Fe-porphyrin. These results validate the strategy of using COF or MOF chemistry to obtain porous networks of molecular catalysts for CO_2 reduction.

In addition to the above hybrid molecular-material systems, some Cu- and Zn-based MOFs can be directly used as electrocatalysts for CO_2 reduction. Hinogami et al. applied a copper rubeanate MOF for CO_2 reduction due to its characteristics of electronic conductivity, proton conductivity, and dispersed reaction sites [157]. Interestingly, the copper rubeanate MOF showed only the HCOOH product in an aqueous electrolyte solution at -1.2 V vs. SHE, whereas a Cu metal electrode generated a range of products. Moreover, the quantity of products was 13-fold higher than that of the Cu metal. Later, Kumar et al. demonstrated a $\text{Cu}_3(\text{BTC})_2$ (BTC = 1,3,5-benzenetricarboxylic acid) MOF film as an efficient electrocatalyst for the selective reduction of carbon dioxide to oxalic acid in N,N-dimethylformamide containing tetrabutylammonium tetrafluoroborate [158]. Recently, Kang et al. deposited Zn-BTC MOF on carbon paper as an electrocatalyst for CO_2 reduction with ionic liquids as the electrolytes [159]. The morphology of the Zn-MOF had a significant effect on performance, and the sheet-like Zn-MOF exhibited the highest activity due to its large electroactive surface areas. By comparing different ionic liquids, it was found that the imidazolium-based ionic liquids with fluorine had the strongest interaction with CO_2 . The excellent combination of Zn-MOF and ionic liquids resulted in the selective reduction of CO_2 to CH_4 (FE > 80%) with a current density of more than 3 mA cm^{-2} at an overpotential of 0.25 V . The integration of MOF-based catalysts and ionic liquids provides an alternative system for improving CO_2 reduction efficiency. Although most of MOFs and COFs possess limit chemical stability, this can be improved by many different approaches, such as utilization of high-valence metal ions or nitrogen-donor ligands with the formation of strong metal-nitrogen bonds, or introduction of porous polymer networks comprising stable covalent C-C, C-H and C-N bonds [160, 161].

7. Summary and outlook

The latest progress on nonprecious metal electrocatalysts for CO₂ reduction is reviewed. In the past several years, great efforts have been made to develop highly efficient nonprecious metal catalysts. Based on composition, the reported catalysts are divided into five categories: metals, partially oxidized metals, metal oxides and sulfides, doped carbons, and organic frameworks. The structures and components of electrocatalysts, catalytic performance, and reaction mechanisms of CO₂ reduction are discussed in detail, and the comparison of different materials is further listed in Tables 1 and 2 to better understand the development of nonprecious metal catalysts.

As a typical nonprecious metal, Cu has been extensively investigated from 0D nanoparticles to 3D hierarchical structures. The particle-size effect in 0D nanoparticles, strain effect in 2D nanolayers, grain-boundary effect in 3D oxide-derived Cu, and facet effect in Cu crystal have been demonstrated to greatly influence the activity of nanostructured Cu catalysts for CO₂ reduction. Furthermore, alloying provides a new means for Cu catalysts to improve activity and selectivity by tuning the binding energy of reaction intermediates. Partially oxidized metal electrocatalysts, typically Sn, Bi, and Co, have exhibited higher performance than their pure metals. Although the mechanism is unclear, the small metastable metal oxide on the surface plays a crucial role in improved activity. However, controlling the oxidation degree of the surface is challenging. It should be noted that the outstanding catalytic activity of partially oxidized 4-atom-thick Co for CO₂ reduction and its synthesis strategy provides new opportunities to tailor the structure and oxidation degree of nanostructured metal catalysts. Among high-valence metal oxides and sulfides, MoO₂ and MoS₂ show the most promising catalytic activity, especially in ionic liquid containing electrolytes.

Except for metal and metal compounds, non-metal or little-metal electrocatalysts have demonstrated unique properties for CO₂ reduction. Typically, N-doped carbons such as carbon nanofibers, carbon nanotubes, graphene, N- or B-doped diamonds, and metal-doped nitrogenated carbons have shown different catalytic behaviors depending on the preparation conditions and electrolyte types. Rational doping will turn inert materials into active catalysts, and it is crucial to control the configuration of heteroatoms in the doped sites. COFs and MOFs have only recently been utilized as electrocatalysts for CO₂ reduction. Incorporating

the molecular catalyst of cobalt porphyrins within COF and MOF frameworks significantly promoted CO₂ to CO with exceptionally high activity and selectivity compared to the existing systems. These hybrid molecular-material systems combine the favorable characteristics of both homogenous and heterogeneous systems and open a new branch of inexpensive and abundant catalysts.

Despite the progress, it seems that CO₂ reduction electrocatalysts are still far from reaching the requirements for commercialization. An ideal electrocatalyst should satisfy the following critical properties: high activity with low overpotential, high selectivity for the desired chemicals, long-term stability, and more importantly, compositions with earth-abundant elements. To achieve these goals, we propose several future research directions:

(1) Exploring novel nonprecious metal electrocatalysts by introducing hierarchical porous structures

Porous materials have exhibited promising catalytic performance in many electrochemical reactions, such as ORR and HER [162–165]. The electrolyte diffusion can be tuned by tailoring the pore size of porous materials from micropore to macropore regions. Macropores (>50 nm) provide facile transfer and diffusion of reactants and products in the reactions over the electrodes, while mesopores (2-50 nm) and micropores (<2 nm) can provide a high surface area to form more active sites with high dispersion. Thus, hierarchical porous materials with integrated properties are desirable for accelerating mass transport and improving CO₂ conversion efficiency. The importance of the porous structure has been demonstrated in noble metals. For example, in a nanoporous Ag catalyst synthesized by a dealloying method, the porous structure not only created an extremely large surface area (ca. 150 times greater than that of polycrystalline silver) but also generated a large number of highly active step sites in the curved internal surface (at least 20 times more active than polycrystalline silver) [35]. More interestingly, in the mesoporous Au catalyst synthesized by colloidal crystal templates, it was found that electrode mesostructuring was a powerful tool for tuning the selectivity of CO₂ reduction catalysis [23]. Diffusional limitations induced by the mesoporous structure could inhibit hydrogen evolution while preserving high rates of CO₂ reduction to CO. Therefore, it is necessary to explore nanoporous nonprecious metal catalysts for the further improvement of catalytic properties.

(2) Optimizing active sites at the molecular level by taking advantage of homogeneous and heterogeneous

Molecule catalysts such as pyridinium and metalloporphyrins hold the promise of improving two of the major challenges present for CO₂ reduction in general: to decrease the overpotential and to increase selectivity toward the desired product [44]. However, homogeneous catalysts are only electroactivated at or near the surface of a conductive electrode, which makes it difficult for them to achieve high current densities. Moreover, there are always the problems of solubility on molecular catalysts in homogeneous solutions. In contrast, heterogeneous electrocatalysis offers the possibility of overcoming these drawbacks. The use of catalysts in heterogeneous form has the potential to eliminate deactivation processes and aggregation of the active catalyst species, providing better control of the chemical surroundings of the active site [156]. Molecular catalysts immobilized on solid supports have shown high current densities compared to free ones. The super performances of COFs and MOFs comprising cobalt porphyrins strongly demonstrate the rationality of this concept. It seems that if the selectivity and catalytic abilities of molecule catalysts could be combined with the features of solid heterogeneous catalysts, the major problems facing electrochemical CO₂ reduction might be solved.

(3) Achieving fundamental understanding of reduction mechanisms by in situ characterization technologies and theoretical calculations

Fundamental understanding of the CO₂ reduction mechanisms in different electrolytes, especially in aqueous systems, is a prerequisite for the development of highly efficient electrocatalysts. Various in situ exploration techniques should be used to directly probe the reduction reactions and gain insights into the reaction mechanism, so as to help identify effective strategies for controlling the structure and components of catalysts. For example, an active intermediate of surface-bound tin-carbonate species on a Sn catalyst was directly observed by using in situ attenuated total reflectance infrared spectroscopy [119]. On a cobalt porphyrin-based MOF catalyst, in situ UV-vis absorbance spectroscopy revealed that the Co^{II} centers are first reduced to Co^I and then the Co^I sites reduce CO₂ [154]. An in situ infrared spectrum illustrated the intermediate OOC-COO of CO₂ reduction in the catalytic process of a B-doped nanodiamond [148]. Therefore, in situ techniques provide a powerful approach for understanding the fundamental reduction processes. Furthermore, the integrated information from these experimental techniques together with

theoretical calculations may bring deeper insights into the interaction of reaction intermediates with the catalyst surface and the relationship of atomic structure, electronic configuration of active sites and catalytic behavior, which would facilitate the rational design of high-performance catalysts.

In summary, electrochemical CO₂ reduction provides an important means to convert environmentally harmful CO₂ into valuable fuels. By using the electricity derived from renewable energy, such as solar and wind power, an artificial photosynthesis process can be achieved, which will open a sustainable route for energy storage and conversion. With continued and extensive efforts in developing novel nanostructured nonprecious catalyst materials, the technology of electrochemical CO₂ reduction will become practical in the near future.

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(b)

CO ₂ Reduction Half Reactions		[V] vs RHE
CO ₂ + H ₂ O + 2e ⁻	→ CO + 2OH ⁻	-0.10
CO ₂ + H ₂ O + 2e ⁻	→ HCOO ⁻ + OH ⁻	-0.03
CO ₂ + 5H ₂ O + 6e ⁻	→ CH ₃ OH + 6OH ⁻	0.03
CO ₂ + 6H ₂ O + 8e ⁻	→ CH ₄ + 8OH ⁻	0.17
2CO ₂ + 8H ₂ O + 12e ⁻	→ C ₂ H ₄ + 12OH ⁻	0.08
H ₂ O Reduction Half Reaction		
2H ₂ O + 2e ⁻	→ 2H ₂ + 2OH ⁻	0.0

Figure 1 (a) Illustration of an artificial way of carbon recycling powered by renewable electricity sources such as wind and solar. (b) Several representative half reactions and reduction potentials of CO₂ reduction reactions, along with that of the HER. Reproduced with permission from Ref. [12]. Copyright 2014 American Chemical Society.

Figure 2 (a) The changes in volume concentrations of gaseous reaction products on the size of Cu nanoparticles, which were normalized using the Cu surface areas. Values for H₂, CH₄, and C₂H₄ are scaled by factors of 0.33, 3, and 5, respectively. (b) The changes in FE for products on Cu nanoparticles. Conditions: 0.1 M KHCO₃, E = -1.1 V vs. RHE, 25°C. (c) Spherical models of Cu nanoparticles with 2.2- and 6.9-nm diameters; surface atoms with different neighbor coordination numbers (CNs) are color coded. (d) Population (relative ratio) of surface atoms with a specific CN as a function of particle diameter. Reproduced with permission from Ref. [57]. Copyright 2014 American Chemical Society.

Figure 3 (a) Scanning electron microscopy (SEM) image of ~7-nm copper nanoparticles supported on a glassy carbon substrate and (b) SEM image of the same nanoparticles following polarization for 10 min at -1.25 V vs. RHE under CO₂ reduction conditions, in which the particle sizes become ~24 nm. (c) SEM image of copper nanoparticles with an average diameter of 52 ± 21 nm and (d) SEM image of the same nanoparticles following polarization for 10 min at -1.25 V vs. RHE, in which the particle sizes become ~25 nm. (e) Proposed mechanism for the electrochemical reduction of CO₂ to methane, including the rate-limiting step (RLS). Reproduced with permission from Ref. [61]. Copyright 2014 American Chemical Society.

Figure 4 (a) Illustration of Cu nanolayers on polycrystalline Pt. (b) Ratios of relative faradaic selectivities for $\text{CH}_4/\text{C}_2\text{H}_4$ on different thicknesses of the Cu layer in an aqueous 0.1 M KHCO_3 electrolyte. Reproduced with permission from Ref. [62]. Copyright 2013 American Chemical Society.

Figure 5 SEM image (a), XRD pattern (b), and XPS spectrum (c) of a Cu foil after annealing at 500°C for 12 h. (d–f) Analogous data for the same electrode after CO₂ reduction at -0.5 V vs. RHE. (g) FEs for CO and HCOOH versus potential and (h) FEs for CH₄, C₂H₄, and C₂H₆ versus potential on annealed Cu and polycrystalline Cu. Reproduced with permission from Ref. [67]. Copyright 2012 American Chemical Society.

Figure 6 (a–c) the (111), (100), and (211) facets of the Cu face-centered cubic crystal. (d) d-Orbital density of states of the above three facets. (e) Comparison of the free energy diagram on the three facets at 0 V vs. RHE in the CH_4 production. Reproduced with permission from Ref. [85]. Copyright 2011 Elsevier.

Figure 7 (a) HRTEM images of Cu-In alloy with fast Fourier transform patterns from the bulk and the surface (inset). (b) Element mapping of the Cu-In alloy: In (green) and Cu (red). (c) Comparison of the current density profiles for OD-Cu and Cu-In alloy. FE analyses of reduced products on OD-Cu (d) and Cu-In (e). (f) Stability test for the Cu-In alloy at -0.6 V vs. RHE in an aqueous 0.1M KHCO_3 electrolyte. Reproduced with permission from Ref. [96]. Copyright 2015 John Wiley and Sons.

Figure 8 (a) SEM image of an anodized Zn electrode and (b) SEM image of the above Zn electrode after electrochemical reduction. (c) FE of CO versus applied potential and (d) FE of CO versus electrolysis time at -1.6 V vs. SCE on as-prepared nanoscale Zn (n-Zn) and Zn foil electrodes. Reproduced with permission from Ref. [101]. Copyright 2015, The Royal Society of Chemistry.

Figure 9 (a) SEM image of the Sn dendrite prepared by electrodeposition of SnCl_2 on a Sn foil in a N_2 -bubbled 1M HCl electrolyte. (b) SEM image of the above Sn dendrite after surface oxidation through heat treatment at 180°C in air. (c) Linear sweep voltammetry polarization curves of the prepared Sn electrodes in a N_2 - (dotted line) or CO_2 -bubbled (solid line) 0.1M KHCO_3 electrolyte at a scan rate of 50 mV s^{-1} . (d) Proposed mechanism for the reduction of CO_2 to formate on a SnO_x/Sn catalyst; “SnO” denotes a Sn^{II} oxyhydroxide species. Reproduced with permission from Ref. [113, 119]. Copyright 2015 John Wiley and Sons. Copyright 2015 American Chemical Society.

Figure 10 (a) SEM image of a Bi-modified GCE. (b) Cyclic voltammetry (CV) curves recorded for Bi-modified and bare GCEs in acetonitrile containing 20 mM EMIM-BF₄. Inset: Bi-modified GCE in acetonitrile without ionic liquid. Reproduced with permission from Ref. [121]. Copyright 2013 American Chemical Society.

Figure 11 (a–c) HRTEM images of the partially oxidized Co 4-atom-thick layers. (d, e) Related schematic atomic models of hexagonal Co (d) and cubic Co_3O_4 (e). (f) Linear sweep voltammetric curves in a N_2 -saturated (dashed line) and CO_2 -saturated (solid line) 0.1 M Na_2SO_4 aqueous solution. (g) FEs of formate at each given potential for 4 h for partially oxidized Co 4-atom-thick layers (red), Co 4-atom-thick layers (blue), partially oxidized bulk Co (violet), and bulk Co (black). Reproduced with permission from Ref. [125]. Copyright 2016 Nature Publishing Group.

Figure 12 (a) CV curves for bulk MoS₂, Ag nanoparticles, and bulk Ag for CO₂ reduction in a solution of 4 mol% EMIM-BF₄ and 96 mol% water. (b) FE of CO and H₂ on bulk MoS₂ at different applied potentials. (c) The current density of CO₂ reduction at -0.764V vs. RHE as a function of water mole fraction in an EMIM-BF₄ electrolyte. Inset is the maximum current density recorded in 96 mol% water. (d) Stability test of the MoS₂ catalyst in different solutions (96, 90, and 0 mol% water). Reproduced with permission from Ref. [132]. Copyright 2014 Nature Publishing Group.

Figure 13 (a) Cross-sectional SEM image and (b) TEM image of NCNT arrays. (c) Onset potential and maximum FE for CO formation as a function of N content in the NCNT arrays. (d) Schematic illustrating CO formation on the NCNTs and free-energy diagram at equilibrium potential for CO₂ reduction on different N defects, including pyridinic, pyrrolic, and graphitic N and pristine CNTs. C, O, and H atoms are represented by gray, red, and white spheres, while pyridinic, pyrrolic, and graphitic N defects are shown using blue, pink, and green spheres, respectively. Reproduced with permission from Ref. [141]. Copyright 2015 John Wiley and Sons.

Figure 14 (a, b) SEM images of GCNT. (c) The stability test on various electrodes at -1.8 V vs. SCE in an aqueous 0.1 M KHCO_3 electrolyte. j_{total} is the geometric current density. Reproduced with permission from Ref. [144]. Copyright 2014 American Chemical Society.

Figure 15 (a, b) SEM images of NDDL/Si RA. (c) Production rates of acetate and formate on NDDL/Si RA electrodes with three N contents of 0.93, 2.12, and 3.68 atom % at -1.0 V vs. RHE. (d) FEs for acetate and formate production at -0.55 to -1.30 V vs. RHE in an aqueous 0.5 M NaHCO₃ electrolyte. Reproduced with permission from Ref. [148]. Copyright 2015 American Chemical Society.

Figure 16 Space-filling structural models of cobalt porphyrin-based 2D covalent organic frameworks, COF-366-M (a) and COF-367-M (b), obtained using Materials Studio 7.0 and refined with experimental PXRD data. SEM images of COF-366-Co (c) and COF-367-Co (d). Reproduced with permission from Ref. [153]. Copyright 2015 The American Association for the Advancement of Science.

Table 1 Representative metal-based catalysts for electrochemical CO₂ reduction

Materials	Synthesis	Electrolyte	Catalytic Performance	Ref.
1.9-nm Cu nanoparticles on glass carbon plates	Inverse micelle encapsulation	Aqueous 0.1 M KHCO ₃	FE _{CO} = 30%, FE _{H₂} = 60–65%, and j_{total} = 48 mA cm ⁻² at -1.1 V vs. RHE	51
Dispersible 7-nm Cu nanoparticles on glass carbon plates	Solvothermal method	Aqueous 0.1 M NaHCO ₃	FE _{CH₄} = 76% and j_{CH4} = 9–10 mA cm ⁻² at -1.35 V vs. RHE Tafel slope = 60 ± 4.2 mV decade ⁻¹	55
Carbon-supported 12-nm Cu nanoparticles on glass carbon electrode	Solution phase reduction	Aqueous 0.1 M KHCO ₃	FE _{C₂H₄} = ~40% at -2.0 V vs. Ag/AgCl	53
50–100-nm Cu particles on Cu foil	Electrodeposition	Aqueous 0.1 M KClO ₄	FE _{C₂H₄} = 36% and FE _{CO} = ~34% at -1.1 V vs. RHE	54
15-nm-thick Cu overlayers on polycrystalline Pt	Electrodeposition	Aqueous 0.1 M KHCO ₃	FE _{CH₄} = ~33% at -1.0 V vs. RHE	56
Cu ₂ O-derived Cu rod arrays on Cu foil	Oxidation and electrochemical reduction	Aqueous 0.5 M NaHCO ₃	FE _{CO} = ~45% at -0.35 V vs. RHE and Tafel slope = 116 mV decade ⁻¹ , FE _{HCOOH} = 33% at -0.75 V vs. RHE	61
CuO-derived Cu nanowire arrays on Cu foil	Oxidation and electrochemical reduction	Aqueous 0.1 M KHCO ₃	FE _{CO} = ~61.8% at -0.4 V and FE _{HCOOH} = 30.7% at -0.6 V vs. RHE, j_{CO} = 1.5 mA cm ⁻²	64
Cu-In alloy (Cu ₁₁ In ₉) on Cu foil	Electrochemical reduction	Aqueous 0.1 M KHCO ₃	FE _{CO} = 90% at -0.6 V vs. RHE with stable operation for 7 h	90
Nanostructured Zn dendrite on Zn foil	Electrodeposition	Aqueous 0.5 M NaHCO ₃	FE _{CO} = 79% and j_{CO} = 14 mA cm ⁻² at -1.1 V vs. RHE Tafel slope = 155 mV decade ⁻¹	94
Zn nanoplate arrays on Zn foil	Anodization and electrochemical reduction	Aqueous 0.5 M NaCl	FE _{CO} = 93% at -1.6 V vs. SCE	95
5-nm nano- SnO ₂ /graphene on glass carbon electrode	Hydrothermal method	Aqueous 0.1 M NaHCO ₃	FE _{HCOOH} = 93.6% and j_{HCOOH} = 10.2 mA cm ⁻² at -1.8 V vs. SCE	108
Hierarchical Sn dendrite with heat treatment at 180°C in air on Sn foil	Electrodeposition	Aqueous 0.1 M KHCO ₃	FE _{HCOOH} = 83.4% at -1.36 V vs. RHE and Tafel slope = 141 mV decade ⁻¹ , production rate = 228.6 μmol h ⁻¹ cm ⁻² with stable operation over 8 h	107
Partially oxidized 4-atom-thick Co sheets on glass carbon electrode	Ligand-confined growth strategy	Aqueous 0.1 M Na ₂ SO ₄	FE _{HCOOH} = 90.1% and j_{HCOOH} = 10.59 mA cm ⁻² at -0.85 V vs. SCE (η = 0.24 V) with stable operation over 40 h Tafel slope = 44 mV decade ⁻¹	119
Rosebud-type Bi thin film on glass carbon electrode	Electrodeposition	Acetonitrile containing 300 mM BMIM-PF ₆	FE _{CO} = 82 ± 12% and j_{CO} = 31 ± 2 mA cm ⁻² at -2.0 V vs. SCE (η = 0.2 V) with the energy efficiencies of Φ _{CO} ≈ 80%	116
Bulk MoS ₂ with Mo-terminated edges	Commercial product	Aqueous 4 mol% EMIM-BF ₄	FE _{CO} = ~98% and j_{CO} = 65 mA cm ⁻² at -0.764 V vs. RHE with stable operation for 10 h	126

Table 2 Representative carbon and organic framework-based catalysts for electrochemical CO₂ reduction

Materials	Synthesis	Electrolyte	Catalytic Performance	Ref.
N-doped carbon nanofibers	Electrospinning	Aqueous 25 mol% EMIM-BF ₄	FE _{CO} = 98% and j_{total} = 16 mA cm ⁻² at -0.573 V vs. RHE with stable operation for 9 h	133
N-doped carbon nanotube arrays	Liquid chemical vapor deposition	Aqueous 0.1 M KHCO ₃	FE _{CO} = 80% and j_{CO} = ~1 mA cm ⁻² at η = -0.18 V with stable operation for 10 h	134
Graphenated carbon nanotube/polyethylenimine composite	Microwave plasma-enhanced chemical vapor deposition (MPECVD)	Aqueous 0.1 M KHCO ₃	FE _{HCOOH} = 87% and j_{HCOOH} = 9.5 mA cm ⁻² at -1.8 V vs. SCE with stable operation for 24 h	138
Metal-doped nitrogenated carbon	Pyrolysis and acid leaching	Aqueous 0.1 M KHCO ₃	FE _{CO} = 80% at -0.5 V vs. RHE	139
B-doped diamond thin film	MPECVD	Methanol solution containing 0.1 M TBAP	FE _{HCHO} = 74% at -1.7 V and FE _{HCOOH} = 15% at -1.5 V vs. Ag/Ag ⁺	141
N-doped nanodiamond on Si rod arrays	MPECVD	Aqueous 0.5 M NaHCO ₃	FE _{CH₃COOH} = ~77% and FE _{HCOOH} = ~14% at -0.8 to -1.0 V vs. RHE Tafel slope _{CH₃COOH} = 77.1 mV decade ⁻¹	142
COF comprising cobalt porphyrins	Imine condensation in solvothermal reaction	Aqueous 0.5 M KHCO ₃	FE _{CO} = 90% and TON = 290000 at -0.67 V vs. RHE (η = -0.55) V with no degradation over 24 h, Tafel slope = 470–550 mV decade ⁻¹	147
Thin film of nanosized MOF comprising cobalt porphyrins	Atomic layer deposition and solvothermal reaction	Aqueous 0.5 M KHCO ₃	FE _{CO} = 76% and TON = 1400 at -0.7 V vs. RHE with stable operation over 7 h Tafel slope = 165 mV decade ⁻¹	149
Cu-MOF	Co-precipitation	Aqueous 0.5 M KHCO ₃	FE _{HCOOH} = 98% and production rate = 13.4 $\mu\text{mol h}^{-1} \text{cm}^{-2}$ at -1.2 V vs. SHE	151
Zn-BTC MOF on carbon paper	Solvothermal reaction and electrophoretic deposition	Ionic liquid of BMIM-BF ₄	FE _{CH₄} = 80.1 $\pm$ 6.6% and j_{total} = 3.1 $\pm$ 0.5 mA cm ⁻² at -2.2 V vs. Ag/Ag ⁺	153

Graphical abstract