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Electrochemical CO2 reduction reaction on copper oxides and metal-nitrogen-carbon catalysts for value-added products generation

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Electrochemical CO_2 reduction reaction on copper oxides and metal-nitrogen-carbon catalysts for value-added products generation

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Abstract

The electrochemical CO_2 reduction reaction (CO_2RR) to value-added products provides an effective and promising approach to mitigate the high CO_2 concentration in the atmosphere and promote energy storage. Among all efficient and selective catalytic materials, Cu oxide catalysts and transition metal-nitrogen-doped carbon materials (M-N-Cs) are well studied because of their high catalysis, good product selectivity, strong stability and cost-effectiveness. Herein, this study summarizes recent and advanced works of CO_2RR on adopting Cu oxide catalysts for alcohols and hydrocarbons generation, as well as the utilization of transition metal-nitrogen-carbon materials for CO formation. We particularly focus on the addition of dopants and the effect of different treatments to control the morphology of Cu oxide catalysts. Furthermore, we also explore the most important reaction active sites (metal-N_x) in Fe-N-Cs and Ni-N-Cs for the selectivity of CO production from CO_2RR. This short review aims to inspire the following development in CO_2RR electrocatalysis.

Keywords:

Carbon dioxide electrochemical reduction reaction; Electrocatalysis; Copper oxide catalysts; Transition metal-nitrogen-carbon catalysts; Value-added products

Introduction

The greenhouse gas carbon dioxide (CO_2) concentration in the atmosphere sustainably increases and reaches to a monthly mean value of 411.76 ppm recently, causing severe environmental and energy issues.[1,2] In order to close the anthropogenic CO_2 cycle, three promising strategies are being developed including decarbonization[3], carbon sequestration and CO_2 conversion[4-5]. Tremendous efforts have been attributed to develop and optimize technologies for converting CO_2 to value-added products.[6,7] Among all the available approaches, electrochemical CO_2 reduction reaction (CO_2RR), which is powered by electricity and uses water as a proton source, has captured high attention because it can activate CO_2 transformation into fuel feedstocks such as carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), methanol (CH_3OH), ethanol (CH_3CH_2OH) and ethylene (C_2H_4), etc. under ambient and environmental friendly conditions.[8,9] The selectivity of these generated products is defined by different reaction pathways and many factors such as the number of electrons and protons transferred, the properties of both cathode electrocatalytic materials and electrolytes, the applied overpotential, etc.[10–13] Given this, it is imperative to explore efficient electrocatalytic materials with high electrocatalysis, strong stability and good products selectivity, in order to lower the high overpotential for converting the thermodynamically stable CO_2 molecule and avoid the competitive side hydrogen evolution reaction (HER).[14] Due to their high efficiency and intrinsically catalytic properties, various metallic electrocatalysts have been studied in terms of their performance for CO_2RR, ranging from Cu (the unique metal for hydrocarbons and alcohols formation) [15] to Au, Ag, Zn (mainly producing CO)[16] and Pb, Hg, In, Sn, Cd, Bi (formate generation).[8,17] Nonetheless, there are still many challenges to reduce the overpotential and control selectivity of the reaction on metallic electrocatalysts, thereby developing more durable, selective and efficient catalysts is of vital importance. In practice, hydrocarbons and alcohols (C_{2+}) produced by Cu-based catalysts have priority because of their high energy density using as liquid fuels compared to C_1 feedstocks.[12,18,19] Therefore, pretreatments of Cu such as oxidization, nanostructuralization and/or bimetal combination can either increase surface roughness or provide subsurface oxygen at the electrocatalyst surface, which can improve CO_2RR performance.[20–23] In this context, Cu oxide electrocatalytic materials have been widely studied in recent years owing to their high selectivity to C_{2+} products.

On the other hand, molecular catalysts such as transition metal-nitrogen-doped carbon materials (M-N-Cs) have played a more and more vital role in CO_2RR[24,25], HER[26] and Oxygen Reduction Reaction (ORR)[27,28] because of their high selectivity and activity, huge catalytic surface area and numerous active sites, inexpensiveness and good stability. Since Varela et al. reported the utilization of Fe/Mn-N-C for the first time on CO_2RR to CO with a Faradaic efficiency (FE) of 80% in 2015[29], there have been several attempts to explore different metals in M-N-Cs to catalyze CO_2RR such as Fe, Co, Ni, Mn, Cu, Cr, etc.[26,30] Among all these metals, Fe-N-C and Ni-N-C show the best electrocatalysis by lowering the overpotential and improving CO selectivity, respectively.[30,31] In the electrochemical reaction systems of M-N-Cs for CO_2RR, each part may have an impact on the overall activity performance such as catalysts properties or electrolyte type.[32–34] However, in this study we only concentrate on reviewing the effect of M-N-Cs on CO_2RR.

It is also worth noting that we only review and discuss the use of Cu oxide-based electrocatalytic materials for the generation of alcohols and hydrocarbons, but leaving out of scope the formation of formic acid/formate[35] and CO[36] from CO_2RR on these materials.

All in all, in this work we focus on the product-selectivity performance via CO_2RR in the past two years on: i) Cu oxide catalysts for multi-carbon products formation, and ii) transition metal-nitrogen-carbon materials for CO production. This short review may provide innovative inspiration for future development directions of CO_2RR.

Cu oxide catalysts for multi-carbon products formation (alcohols and hydrocarbons)

Copper seems to be the unique metal which shows in literature the possibility of converting CO_2 into multi-carbon products (hydrocarbons and alcohols) with moderate efficiencies.[37] Nevertheless, it suffers some drawbacks such as low products selectivity and catalytic stability. In this context, the application of Cu oxide based electrocatalytic materials appears to improve process performance owing to morphological features such as roughness. Herein, therefore, we summarize recent research on Cu oxide electrocatalysts with high catalytic efficiency and activity (Table 1). Since Frese et al. firstly reported that the oxidized Cu electrodes can be used to convert CO_2 to methanol in aqueous solution,

[38] several authors have extensively investigated the use of Cu oxide surfaces in CO_2RR for alcohols production. For example, Manna et al. reported that synthesized cuprous oxide (Cu_2O) nanocatalysts can selectively produce methanol with a maximum Faradaic efficiency (FE) of 47.5% at a current density of 7.8 mA cm^{-2} in comparison with metallic Cu nanocatalysts, where methane and ethylene were the main products observed.[39] Besides, the treatment of Cu_2O with Prussian Blue analogue (K-PBA) to form core-shell nanocubes (Cu_2O@K-PBA) increases C_{2+} products ratios with FE of 23.9% (ethylene 10.8%, ethanol 3.6% and n-propanol 9.5%). The authors attributed this improvement to the ability of K-PBA for changing the intrinsic energetics of Cu_2O.[40] Moreover, Gao et al. demonstrated that theoretical methods such as density functional theory (DFT) may provide a new perspective to prove the mechanism of CO_2RR to methanol on Cu_2O. [41] In this research, DFT was used to investigate the formation of the helpful reaction intermediate CH_3OH*-OH*, as well as figuring out the influence of catalyst surface morphology and solvation during methanol formation process. Furthermore, they also strengthened the “variation trend of charge distribution” leading to the choice of “minimum-energy pathway”.

Likewise, a lot of efforts have been dedicated to develop and improve Cu oxide electrocatalysts for CO_2RR to hydrocarbons (ethylene and methane) from several aspects such as the addition of heterogeneous dopant to Cu oxides, the change of catalysts surface morphology, the increase of electrocatalytic active sites, the control of electrolyte pH, and the application of proper potentials and currents for an improved behavior. For instance, Boron-doped oxide-derived Cu greatly catalyze CO_2 to C_2 products because Boron impacts on stabilizing Cu^+ species. [42] In this regard, Merino-Garcia et al. also illustrated the effect of Zn on stabilizing Cu^+ atoms as well as suppressing H_2 evolution in Cu oxides/ZnO-based electrocatalytic surfaces for the production of hydrocarbons from CO_2RR, leading to an outstanding performance toward ethylene with FE as high as 91.1%. [43] Similarly, Sun et al. adopted N-doped carbon (N_xC) as a carrier of CuO by catching more CO_2 to increase ethylene selectivity. Compared to CuO loaded on carbon black, the former shows better ethylene selectivity and activity. This research provides a cost-effectiveness and efficient method to increase catalytic activity and reaction selectivity by combining CuO and CO_2 capture materials.[44] In addition, the utilization of ionic liquid functionalized graphite sheets is studied for controlling the morphology and size of Cu_2O nanocubes (Cu_2O/ILGS).[45] Cu_2O/ILGS are able to inhibit the latter’s aggregation, hence enlarging the surface active sites for CO_2RR, reaching a high ethylene efficiency. Moreover, Cu oxide catalysts may sometimes transform their morphology during the electrocatalytic process. It is reported that Cu_2O nanoparticles on carbon can undergo fragmentation to smaller pieces during CO_2RR, thus increasing compact morphology and grain boundaries, which can facilitate the selectivity and activity toward C_{2+} products (Fig.1a).[46] In particular, grain boundaries play a crucial role for faster oxygen diffusion and oxide nucleation in Cu oxides catalyst for Cu reoxidation. As shown in Fig.1b, Cu nanomaterials with a high number of grain boundaries can provide more spaces and active sites for O_2 diffusion and adsorption, accelerating the reoxidation of Cu. The numerous grain boundaries in this catalyst are responsible for promoting C_2/C_3 products.[47] Yu et al. evaluated the effects of solution pH and CO_2 mass transfer for CO_2RR at Cu_xO surfaces.[48] They proved the alkaline environment benefits surface oxygen as well as C_2 products (ethylene and ethanol). The authors also described the fast CO_2 mass transfer in gas state using gas diffusion electrodes (GDEs) in comparison with aqueous solution, in which the reaction kinetics is limited by the low CO_2 solubility and diffusion coefficient. This concept is in accordance with the theory in the literature.[43] Interestingly, Yeo et al. demonstrated the major impact of potentials and currents on reaction selectivity at Cu oxide catalysts.[49] In this paper, the authors illustrated that product selectivity relies on surface roughness: methane, ethylene, alcohols, CO or formate can be gained successively as the surface roughness aggravate. As shown in Fig. 1c, 1d and 1e, the control of the applied potential (ranging from -0.45V to -1.3 V vs. RHE) is crucial to tailor the selectivity of CO_2RR in order to select proper products efficiently. Furthermore, the method of isotopic labelling, which can trace the products composition and uncover the reaction mechanism by supplying isotopic reactant, provides information to understand why different products are generated during CO_2RR.[50] Given a mixture of ^{13}CO and $^{12}CO_2$, the CO_2RR should have different $^{12}C/^{13}C$ distribution in each kind of product formed on different active sites. It is finally reported that three different existing active sites are responsible for the formation of ethylene, ethanol/acetate and 1-propanol, respectively, which directs a way for high selectivity in CO_2RR research.

Overall, tremendous synthesis and treatment methods have been developed and proved to be efficient for CO_2RR to alcohols and hydrocarbons on Cu oxides catalysts. However, it’s still a challenge for the researchers of revealing the mechanisms and select specific and unique products.

Transition Metal-Nitrogen-Carbon materials for CO_2RR to carbon monoxide

As mentioned above, Cu oxide materials mainly boost the catalytic activity for promoting the formation of C_{2+} products. For CO generation, however, M-N-Cs (Fig. 2a) have been widely studied in literature due to their numerous active sites of synergistic M-N_x moieties on the huge surface area, which can modify the binding energy of the chemical intermediates related to CO_2RR. Unfortunately, these transition metals have excellent and prior catalysis on competing side HER rather than CO_2RR. However, when metal arrangement goes into a single atom structure, its electrocatalysis role on CO_2RR can be greatly enhanced due to the electronic environment, which has drawn a lot of attention recently.[33] Among all research studies about M-N-Cs, one trend is focused on the reaction mechanism of Fe-N-Cs as efficient catalyst for CO formation due to their superior high efficiency. The comparison between CO FEs at different metals-N-Cs electrocatalysts as a function of the applied potential is shown in Fig.2b. For instance, Yang et al.[51] reported the utilization of porous nanosphere Fe-N-C for CO_2RR to CO, achieving an interesting high FE around 90%, where the key aspect in terms of active sites was demonstrated to be the synergistic role between the single-atom Fe-N_4 moieties and adjacent C. In addition, rotating disk electrode (RDE) was used to carry out linear sweep voltammetry (LSV) analyses in order to measure the electrochemical response in the presence or absence of Fe center (Fig.2c). By comparison, the presence of Fe center notably enhances the catalytic performance, which leads to the conclusion that the Fe atom plays a vital role in the active sites of the electrocatalytic material for an efficient CO_2RR. Furthermore, thiocyanate ions (SCN^-) has been known to coordinate with Fe because of a strong affinity, the addition of SCN^-into the electrolyte can poison Fe atoms by capturing the latter, leading to a decrease in the FE to CO. In this context, Shao et al. went a step further via DFT calculations, where they strengthened the fact that the real active sites are the Fe-N_4 moieties surrounding by defective carbon through a proof of poisoned Fe atoms by CO inhibiting the following reaction, because this kind of moieties possesses the smallest Gibbs free energy (Fig.2d). Surprisingly, this research reports an extremely small overpotential of 90 mV, which is in the top level among Fe-N-C groups.[52] On the contrary, Zhou et al. stated that Fe-N-C materials derived from $Fe(SCN)_3$ (denoted as SMFeSCN) are responsible for an improved FE to CO up to 99%, in comparison with the performance reached on SMFe (without SCN). The authors attributed this enhancement to the numerous microporous nanostructures of SMFeSCN, which increases the CO_2 local concentration.[53] Based on the outstanding catalysis of

Fe-N-C, Li et al. doped sulfur (S) on it, achieving a FE for CO generation of 98%.[54] The dopant S is embedded in the graphitic layer together with Fe-N_4, thus increasing the activity of the latter by changing its Fermi level and charge density (Fig.2e and 2f).

On the other hand, Ni-N-Cs-based electrocatalysts exhibit attractive performance for CO_2RR conversion to CO as well.[31] Unlike Fe-N-Cs catalysts, that are beneficial for lowering the overpotential of CO formation, Ni-N-Cs materials are popular mainly because of their high CO selectivity. This fact is mainly attributed to the presence of Ni single atoms within the Ni-N-Cs electrocatalysts.[33] Based on this theory, we summarize and study the works where high FEs to CO are achieved at Ni-N-Cs electrocatalysts, noting that the most important active sites are located in the Ni-N_x moieties, which can act either in a synergistic way with different N or be affected by the surrounding environment. Sun et al.[55] and Liu et al.[56] strengthened the significance of pyrrolic N in the synergistic effect with Ni-N_x by controlling nitrogen precursors to tune the catalytic activity for FEs of 96.5% and 80% to CO, respectively. In addition, Ni-N_x moieties are various depending on the number and species of N and the surrounding environment, causing different catalytic activities. Based on this, DFT is used to analyze the most valuable active site Ni-N_x.[57,58] In this regard, with synthesized Ni-N-doped carbon nanotubes, Sun et al.[57] calculated the free energies of the intermediate *COOH on Ni@N_3 (pyrrolic), Ni@N_3 (pyridinic) and Ni@N_4, respectively. They found that Ni@N_3 (pyrrolic) is the most efficient active site due to its lowest free energy (Fig. 3a). Besides, Li et al. developed rhombic dodecahedron shape of Ni-N-C in order to compare the behavior of the catalysts in the presence/absence of the metal center Ni. In this regard, Ni-N-C showed much better electrocatalysis than N-C in terms of high FE toward CO (Fig.3b) and more positive onset potential (Fig.3c). Nevertheless, they found that Ni-N_4 (Ni-N_4-C_{10}) matters in the catalysis reaction, that is, in other words, the edge-located Ni-N_{2+2} (Ni-N_{2+2}-C_8) is responsible for the high selectivity to CO (96% FE) rather than Ni-N_4 in bulk Ni-N-C rhombic dodecahedron (Fig.3d).[58] These conclusions may provide new insights into the synthesis of specific Ni-N-C electrocatalysts with desired properties for an improved CO_2RR-to-CO process efficiency and selectivity.

Last but not the least, it should be mentioned that Cu-N-Cs also show a remarkable ability to obtain multi-carbon products like previously discussed on Cu oxide catalysts. Several interesting studies of

CO_2RR on Cu-N-Cs toward ethylene,[59,60] ethanol [61] and formate and acetate [62] can be found in literature in recent years.

In conclusion, M-N-Cs catalysts are promising for CO_2RR due to their enhanced electrocatalytic activity compared to metal-free N-doped carbon materials, especially Fe-N-Cs and Ni-N-Cs which shown excellent performance for converting CO_2 to CO at high FEs.

Conclusions

In summary, the most recent works on Cu oxide catalysts and transition metal-nitrogen doped carbon materials for the electrochemical CO_2 reduction reaction into value-added products are reviewed. Different treatments and modifications such as morphology control and increase surface roughness of Cu oxides catalysts can dramatically enhance the performance of CO_2RR to C_{2+} products (alcohols and hydrocarbons), which are in need for energy storage. Moreover, Fe-N-Cs and Ni-N-Cs materials are proved to be promising and efficient in catalyzing CO_2 to CO with outstanding FEs, on account of the active sites Fe-N_x and Ni-N_x playing the most vital roles , which may also synergy with surrounding N and carbon. Yet, many challenges remain to be explored including tailoring the target products, figuring out the mechanisms for reaction selectivity, simplifying synthesis process of catalysts. This review may provide new insights for the development of efficient, selective, durable and stable electrocatalysts for an improved CO_2RR performance toward target products.

Conflict of interest statement

The authors declare no interest conflict.

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Table 1. Comparison of the performance of different Cu oxide catalysts recently reported in literature for CO_2RR.

Fig. 1 (a) HRTEM image for Cu based nanoparticles after 10 h of CO_2RR. Adapted with permission from ref [46]. Copyright 2019 American Chemical Society. (b) Illustration of rapid reoxidation of oxide-derived (OD) Cu on grain boundaries (GB). Reprinted with permission from ref [47]. Copyright 2018 John Wiley and Sons. (c) (d) (e) Faradaic efficiency of methane, ethylene and ethanol, carbon monoxide and formate on different catalysts at different potentials, respectively. Different catalysts Cu-10, CuO-1, CuO-10, and CuO-60 are Cu based catalysts electrodeposited for 1 min, 10 min and 60 min, respectively, which are shown in color of orange, green, red and blue, respectively. Error bars in (c)–(e) represent the standard deviations of three independent measurements. Open access article ref [49]. Distributed under the terms of the Creative Commons CC BY license.

Fig. 2 (a) General synthesis strategy of M-N-C catalysts and their obtained structure. Reprinted with permission from ref [24]. Copyright 2019 American Chemical Society. (b) CO FEs at different metal-N-C catalysts. Reprinted with permission from ref [30]. Copyright 2018 Elsevier. (c) LSV curves of Fe−N−PC, op−Fe−N−PC and N−PC in CO_2-saturated 0.5 $mol\cdot L^{-1}$ $KHCO_3$ solution (scan rate = 10 mV/s). Reprinted with permission from ref [51]. Copyright 2019 American Chemical Society. (d) Gibbs free energy diagrams of CO_2RR on different sites by DFT. Reprinted with permission from ref [52]. Copyright 2019 American Chemical Society (e) S doped Fe-M-C structure. (f) Comparison of FEs to CO in 0.1 M $KHCO_3$ aqueous solution on different catalysts. Reprinted with permission from ref [54]. Copyright 2019 Elsevier.

Fig.3 (a) Free energy diagram of CO_2RR to CO on Ni@N_4, Ni@N_3 (pyrrolic) and Ni@N_3 (pyridinic). Reprinted with permission from ref [57]. Copyright 2019 John Wiley and Sons. (b) CO and H_2 Faradaic efficiency and (c) CO partial current density for N–C and Ni–N–C. (d) Initial and final states for the COOH dissociation reaction on Ni–N_4–C_{10} and Ni–N_{2+2}–C_8 sites. Reprinted with permission from ref [58]. Copyright 2019 Royal Society of Chemistry.

Table 1.

Cu oxide catalysts	Electrolyte	E / V vs. RHE	Target products	FE (%)	Ref
Cu_2O NP	$KHCO_3$	-2.0 V vs. SHE	CH_3OH	47.5	[39]
Cu_2O@K-PBA	n.a.	-1.11	C_2H_4	23.9	[40]
B-OD Cu	0.1 M $KHCO_3$	-1.05	C_2	48.2	[42]
Cu oxides/ZnO	0.1 M $KHCO_3$	-2.5 V vs. Ag/AgCl	C_2H_4	91.1	[43]
CuO/N_xC	0.1 M $NaHCO_3$	-1.25	C_2H_4	36	[44]
Cu_2O/ILGS	0.1 M $KHCO_3$	-1.15	C_2H_4	31.1	[45]
Cu_2O NP/C	0.1 M $KHCO_3$	-1.1	C_2/C_3	74	[46]
OD Cu	0.1 M $KHCO_3$	-1.0	C_2/C_3	60	[47]
Cu_xO	2.0 M KOH	-1.17	C_2	40	[48]
Different OD Cu	0.1 M $KHCO_3$	-0.9 ~ -1.1	C_2	48	[49]
		-1.15	CH_4	40	
		-0.5	CO	46	
		-0.6	$HCOO^-$	35	

Abbreviations: Nanoparticles (NP), Prussian Blue Analogue (PBA), B-OD (Boron-doped oxide-derived) and Ionic Liquid functionalized Graphite Sheets (ILGS).

Fig.1

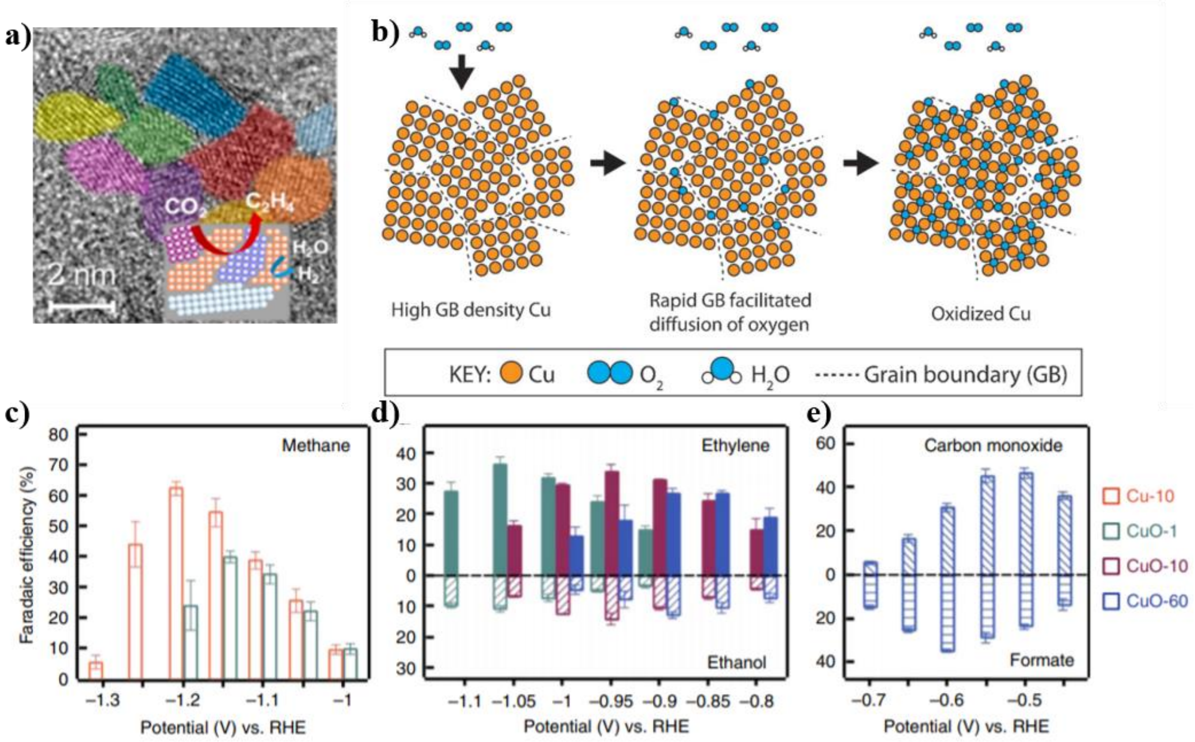

a)
2 nm
CO2
C2H4
H2O
H2
b)
High GB density Cu
Rapid GB facilitated diffusion of oxygen
Oxidized Cu
KEY: Cu O2 H2O Grain boundary (GB)
c)
Methane
Faradaic efficiency (%)
80
70
60
50
40
30
20
10
0
−1.3
−1.2
−1.1
−1
Potential (V) vs. RHE
d)
Ethylene
Ethanol
40
30
20
10
0
10
20
30
−1.1
−1.05
−1
−0.95
−0.9
−0.85
−0.8
Potential (V) vs. RHE
e)
Carbon monoxide
Formate
60
40
20
0
20
40
−0.7
−0.6
−0.5
Potential (V) vs. RHE
Cu-10
CuO-1
CuO-10
CuO-60

Fig.2.

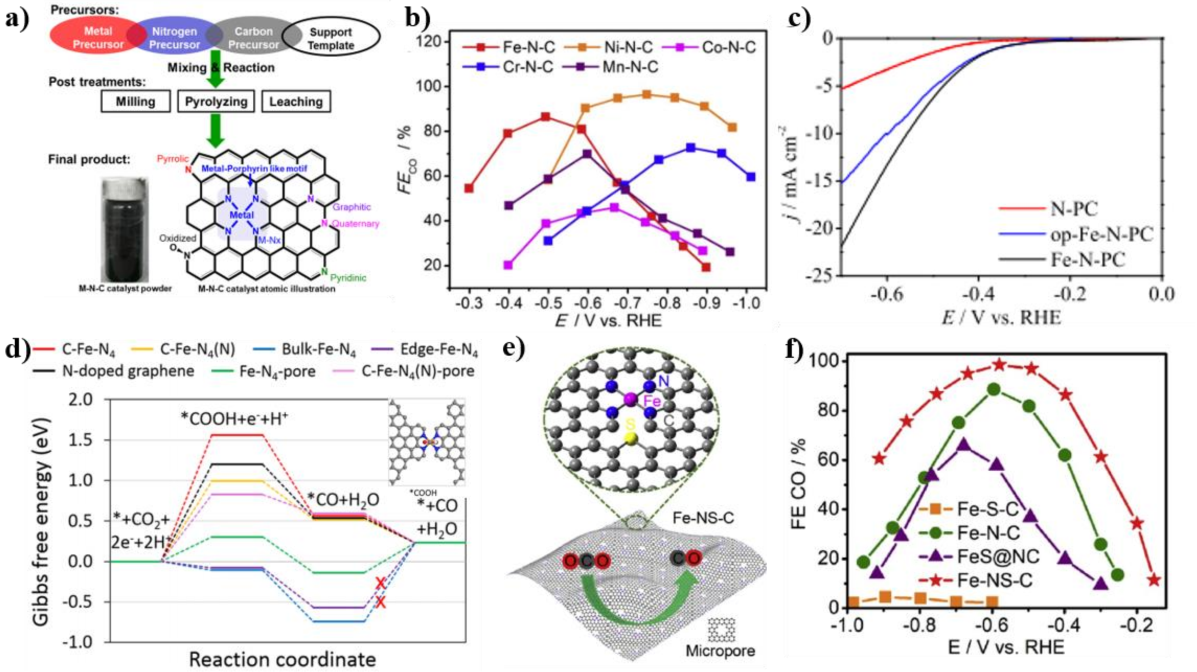
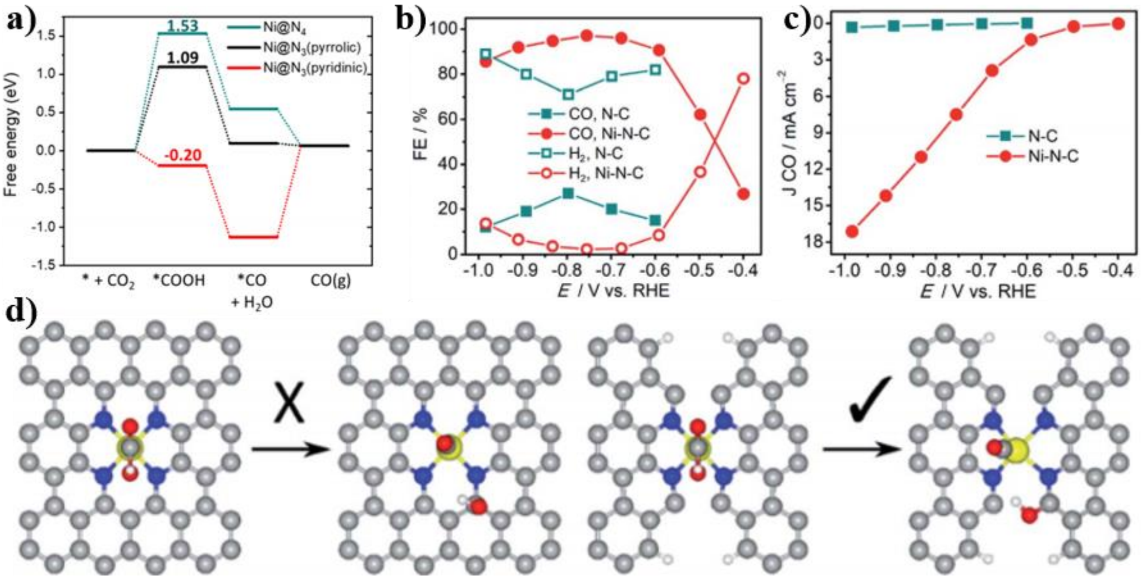

a)
Precursors:
Metal Precursor
Nitrogen Precursor
Carbon Precursor
Support Template
Mixing & Reaction
Post treatments:
Milling
Pyrolyzing
Leaching
Final product:
Pyrrolic
Metal-Porphyrin like motif
Metal
M-Nx
Graphitic
Quaternary
Oxidized
Pyridinic
M-N-C catalyst powder
M-N-C catalyst atomic illustration
b)
Fe-N-C
Ni-N-C
Co-N-C
Cr-N-C
Mn-N-C
FE_{CO} / %
120
100
80
60
40
20
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
E / V vs. RHE
c)
0
-5
-10
-15
-20
-25
j / mA cm^{-2}
N-PC
op-Fe-N-PC
Fe-N-PC
-0.6
-0.4
-0.2
0.0
E / V vs. RHE
d)
C-Fe-N$_4$
C-Fe-N$_4$(N)
Bulk-Fe-N$_4$
Edge-Fe-N$_4$
N-doped graphene
Fe-N$_4$-pore
C-Fe-N$_4$(N)-pore
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
Gibbs free energy (eV)
*COOH+e$^-$+H$^+$
*+CO$_2$+
2e$^-$+2H$^+$
*CO+H$_2$O
*COOH
*+CO
+H$_2$O
X
X
Reaction coordinate
e)
N
Fe
C
S
Fe-NS-C
O C O
C O
Micropore
f)
FE CO / %
100
80
60
40
20
0
Fe-S-C
Fe-N-C
FeS@NC
Fe-NS-C
-1.0
-0.8
-0.6
-0.4
-0.2
E / V vs. RHE

Fig.3.


a)
Free energy (eV)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
1.53
1.09
-0.20
Ni@N$_4$
Ni@N$_3$(pyrrolic)
Ni@N$_3$(pyridinic)
* + CO$_2$
*COOH
*CO + H$_2$O
CO(g)
b)
FE / %
100
80
60
40
20
0
CO, N-C
CO, Ni-N-C
H$_2$, N-C
H$_2$, Ni-N-C
-1.0
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
E / V vs. RHE
c)
J CO / mA cm^{-2}
0
3
6
9
12
15
18
N-C
Ni-N-C
-1.0
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
E / V vs. RHE
d)
X
✓

Appendix

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest

** of outstanding interest

*[5]	This review comprehensively summarized metal–organic complexes, metals, metal alloys, inorganic metal compounds and carbon-based metal-free nanomaterials for CO_2 reduction.
*[11]	Different abbreviation systems for denoting imidazolium-based room temperature ionic liquids (RTILs) used for CO_2 electrochemical conversion are reviewed about their physicochemical properties.
**[24]	This review analyzed various factors and described DFT directing experiments on the activity and selectivity of M-N-Cs.
**[33]	This paper strengthened the importance of single atoms Ni for CO_2RR in several aspects and demonstrated different performance of various Ni active sites.
**[44]	This paper described cubic Cu_2O crystalline particles electrochemically fragmentate into smaller particles and the grain boundaries generated can promote C-C coupling in CO_2RR.
**[45]	This article demonstrated faster oxygen diffusion and oxide nucleation in Cu oxides catalyst for Cu reoxidation on grain boundaries.
**[47]	The authors illustrated products selectivity relies on surface roughness and revealed the effects of applied potential on the products selectivity of CO_2RR.
**[53]	This paper showed an outstanding Faradaic efficiency (99%) for CO and studied the stable catalytic performance of the Fe-N-CSCN even with the addition of metal-ion impurities because of the numerous separated active sites.
*[54]	This paper proved the dopant sulfur in Fe-N-C structure can enhance the Faradaic efficiency to CO (98%).
**[58]	This paper adopt DFT calculation to compare the active sites of $Ni\text{-}N_4\text{-}C_{10}$ and $Ni\text{-}N_{2+2}\text{-}C_8$ and found that the edge-located $Ni\text{-}N_{2+2}\text{-}C_8$ are responsible for the good performance of CO_2RR because of lower free energy.