Abstract: Electrochemical CO₂ reduction reaction (CO₂RR) provides a promising approach to curbing harmful emissions contributing to global warming. However, several challenges hinder the commercialization of this technology, including high overpotentials, electrode instability, and low Faradic efficiencies of desirable products. Several materials have been developed to overcome these challenges. This mini-review discusses the recent performance of various cobalt (Co) electrocatalysts, including Co-single atom, Co-multi metals, Co-complexes, Co-based metal–organic frameworks (MOFs), Co-based covalent organic frameworks (COFs), Co-nitrides, and Co-oxides. These materials are reviewed with respect to their stability of facilitating CO₂ conversion to valuable products, and a summary of the current literature is highlighted, along with future perspectives for the development of efficient CO₂RR.

Keywords: CO₂ conversion; electrocatalysts; cobalt catalysts; MOFs; ECO₂RR

1. Introduction

The excessive combustion of fossil fuels has caused massive carbon dioxide (CO₂) emissions, leading to rapid global environmental changes such as global warming, air pollution, desertification, acid rains, rise in sea levels, and extreme weather conditions [1]. The threats to human life and the environment due to high CO₂ emissions are increasing day by day with growing energy demands. The kneeling curve from the Mona lova observatory shows a drastic increase in CO₂ concentration. In May 2021, the CO₂ concentration was 419.13 ppm which is caused due to enormous emission of CO₂ into the atmosphere (40 billion metric tons per year). According to the Global Warming Potential (GWP) updates by the United States Environmental Protection Agency (EPA), CO₂ has a GWP value of 1, which is lower than the value of CH₄, N₂O, chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), and other greenhouse gases. However, the CO₂ absorption energy is much higher as it has remained for thousands of years in the atmosphere compared to other...
greenhouse gases, reflecting the severe contribution of CO$_2$ in global warming. To prevent these harmful impacts, the Paris Climate Agreement was signed by United Nations to limit the rise in temperature to 2 °C in the 21st century above the pre-industrial levels and pursuing to reduce it to 1.5 °C. However, the predictions by the US Energy Information Administration state that the use of fossil fuels is expected to increase until 2040, which will cause the global temperature to rise more than 2 °C. CO$_2$ gas emission should be equal to the amount of CO$_2$ consumed. Therefore, alternatives to reduce global CO$_2$ emissions and CO$_2$ conversions to less harmful products are highly needed to cope with global warming issues in time [2,3].

Several carbon capture and utilization methods are implemented to mitigate CO$_2$ concentration in the atmosphere and overcome its environmental challenges [4–8]. The main strategies to reduce CO$_2$ emissions deal with the circular carbon economy (CCE), a holistic approach that consists of Reduce, Reuse, Recycle and Remove (4Rs) of CO$_2$. The reuse of CO$_2$ is categorized to search for low carbon energy alternatives such as wind, solar and hydro energy for replacing fossil fuels. Another approach is geological sequestration, a promising strategy to provide a low carbon energy future [9–11]. Still, there is uncertainty about stored CO$_2$ for a long time, and it might have leakage issues. Another approach is recycling, and utilizing CO$_2$ into other useful chemicals is the most attractive strategy to reduce CO$_2$ emissions [12–14]. Catalysis plays a vital role in our daily life. Various types of catalysts have been reported for the conversion of waste into useful products, including zeolites [15–29], metal and metal oxides [30–42], nitrides [43–51], carbon-based catalysts [52–63], metal complexes [64–72] or highly porous metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) [5,73–80]. The synthesis of supported catalysts methods has also been reviewed recently [81]. We observed the superior behavior of cobalt in catalysis, especially in electrocatalysis. Cobalt catalysts are very important due to their extensive applications in many industrial processes, such as Fisher–Tropsch synthesis [82,83] and CO$_2$ conversion [84]. Electrocatalytic CO$_2$ reduction reaction (CO$_2$RR) is a promising strategy due to its easy operating system, simple constructions, operational at neutral pH, ambient temperature and atmospheric pressure, and low energy utilization to produce valuable chemicals and fuels such as formic acid, methane, ethanol, and carbon using renewable electricity. Therefore, CO$_2$RR coupling with renewable energy sources can effectively achieve a carbon-neutral energy cycle and hydrocarbon products with high activity, stability, and selectivity [85,86]

Many expensive noble-metal electrocatalysts such as Au, Ag and Pd-based electrocatalysts have been employed for CO$_2$RR, exhibiting high electrocatalytic performances, selectivity, and stability with low overpotential [87]. However, their wide use applications for CO$_2$RR have been hampered by their high cost. Therefore, explorations to find the noble metal-free efficient catalysts for CO$_2$RR have led to the discovery of various catalysts such as different types of metals, metal oxides, supported single atoms and single-site catalysts, transition metals supported/embedded on graphene, bimetal and metal/carbon hybrids, porphyrin like structures functionalized by metals, MOFs, colloidal nanocrystals and doped nanostructures [88–101]. Current challenges to the electrocatalysts are their stability, the reduction onset potential, current density, and Faradic efficiency. Another challenge is to find an electrocatalyst that is active for the CO$_2$RR to produce useful products, while competing the hydrogen production reaction. The high reduction over potential leads to a waste of energy and a significant H$_2$ evolution reaction (HER), a significant side reaction that prevails over the CO$_2$RR.

Co-based materials have many advantages over others because as a popular metal, Co belongs to the group VIII-B of the periodic table having unique features like high electrical conductivity, thermal stability, unique electronic features, chemical stability, and high catalytic performances, which makes co-based catalysts as promising materials for CO$_2$RR applications. Cobalt as an earth-abundant transition metal is a splendid alternative to noble metals such as Pt, Ir, Ru, etc. For CO$_2$RR, Co has been used as a prominent source as noble metal-free electro/photocatalysts due to fascinating properties such as loosely bonded
d-electrons and therefore readily available multiple oxidation states (Co(0), Co(I), Co(II), Co(III) and Co(IV)). Moreover, it is found that a transition from Co(II) to Co(I) is involved at the intermediate state for CO$_2$ reduction. Hence, high activity, outstanding stability and product selectivity are achieved through Co-based catalysts for CO$_2$ reduction [84,102]. Cobalt is more reactive than other earth-abundant metals due to the possession of modest CO$_2$ adsorption and d-band closeness to the Fermi level [103]. Co-based catalysts have been explored as effective cathode materials for electroreduction of CO$_2$ to CO exhibiting high activities and selectivity [104]. For CO$_2$ photoreduction, Co metal sites in Co-based MOFs offer the traps for electrons for facilitation in electrons-holes separation, thus providing a longer life for electrons for the reduction reaction. Co is found to be an important stabilizer for major intermediates in CO$_2$ reduction [84,103]. Co-based materials have applications in various other fields such as energy storage, catalysis, and thermopower. Co-based materials (i.e., Na$_x$CoO$_2$) play a critical role in cathode and anode materials for Na-ion batteries. Likewise, LiCoO$_2$ has been regarded as one of the most commercialized cathode materials for Li-ion batteries. Cobalt oxides and cobalt chalcogenides exhibit a high theoretical capacity for sodium storage [105]. Thus, cobalt has been reported as an important center for CO$_2$ reduction [40,46,106–109].

The previous state-of-the-art review articles [84,110–115] have discussed ECO$_2$RR more extensively. The ECO$_2$RR using cobalt-based materials has gained considerable interest. Figure 1 shows the vast available literature on cobalt electrocatalysts and cobalt catalysts for CO$_2$RR. Therefore, this review is designed to summarize cobalt-based electrocatalysts’ current progress in converting CO$_2$ into valuable products. Emphasis is given to cobalt-based MOFs, COFs, cobalt complexes, cobalt oxides, cobalt nitrides, cobalt multi-metals and single cobalt atom catalysis.

Figure 1. Published literature on cobalt electrocatalyst and cobalt catalysts for CO$_2$ conversion. Source SciFinder, keyword: cobalt electrocatalyst, cobalt catalyst for CO$_2$ reduction.

2. Cobalt Catalysts for CO$_2$ Reduction

2.1. Cobalt-Based Single-Atom Catalysts (SACs) for CO$_2$RR

CO$_2$ reduction reaction (CO$_2$RR) catalysts have challenges of high overpotential, low Faradaic efficiency, low current density and lack of long-term stability. However, single-atom catalysts (SACs) are used for CO$_2$RR with great importance. Studies show that SACs for CO$_2$RR are of two categories based on their synthesis route: i) organometallic precursor
pyrolysis such as MOFs; ii) loading of the metal precursor directly onto the support, which are followed by heat and acids treatment to get rid of the excess nanoparticles as shown in Figure 2. The Co precursor was dispersed with the polymer (Pluronic F127) and the colloidal silica, then the mixture was pyrolyzed and the template was etched by acid treatment to obtain the Co-SAS/HOPNC. Uniform hierarchical and atomic sites of cobalt dispersed in the carbon matrix were observed by the BET. SEM and TEM and the elemental analysis confirm the presence of the Co, N and C.

The CO\textsubscript{2}RR was investigated by using a single-atom cobalt catalyst (Co-Typ-C) by Hou and coworkers \cite{116} via the pyrolysis of Co-terpyridine (TPY) organo-metallic complex. The catalyst exhibited excellent acidity with CO Faradaic efficiency (FE) of >95% from −0.7–1.0 V (vs RHE). The catalysts without Co or Tpy ligand do not exhibit high CO FE. A virtual flue-gas with 15% CO\textsubscript{2} was utilized as a source of CO\textsubscript{2} to verify the catalyst’s efficacy, revealing that the CO FE was reserved at ~90% at a potential of −0.5 V (vs RHE). The CO partial current-density was promoted to 86.4 mAcm\textsuperscript{−2} and CO FE reached over 90% at a cell voltage of 3.4 V. The study indicates that a regular single atom Co-N\textsubscript{4} site generally contributed to the good performance of the catalyst for CO\textsubscript{2} reduction. A study by Shi et al. \cite{117} shows that the atomic Co species (ACS) modified 2D telluriumnanosheet (Te Ns) act as an active single atom Co catalyst for CO\textsubscript{2} reduction under visible light absorber. The ACS catalytic site serves as efficient electron transfer built via the coordinated Co center with five Co-Ô. Their finding reveals that the strong mutual interaction among Te Ns and ACS altered the electronic structure of Te Ns’, which induced the introduction of intermediate energy states acting as trap centers. The CO\textsubscript{2} conversion reactions via the aid of \cite{118} Cl\textsubscript{3} complex as the light absorber gives the CO product amount of ~52.3 µmol/L, which has the best performance compared to the conventional catalysts under similar conditions.

Huang and coworkers \cite{120} fabricated partially-oxidized cobalt nanoparticles (5 nm) dispersed on a single-layered nitrogen-depend graphene catalyst (PO-5 nm Co/SL-NG) as shown in Figure 3. They revealed that the catalyst was efficient for selective CO\textsubscript{2}
electrocatalytic reduction to MeOH in a 0.1 M NaHCO$_3$ electrolyte under mild conditions. A Faradaic efficiency of about 71% was reported for MeOH at $-0.9$ V (vs. SCE) and possessed a high electrocatalytic current density of 4 mAcm$^{-2}$ with a yield of 1.0 mmoldm$^{-3}$h$^{-1}$. A low corresponding over the potential of $-280$ mV was observed while Faradaic efficiency for MeOH remain 23.3% at $-1.0$ V (vs SCE) at a current density of 10 mAcm$^{-2}$. The catalyst was stable even after 10 h of the CO$_2$ electro-reduction. They also propose a mechanism for CO$_2$ reduction to methanol, as shown in Figure 3g. The support (SL-NG) promotes CO$_2$ and multiple proton-transfer steps to produced methanol. Cobalt provides a synergistic effect between Co and supports to allow multiple proton- and electron-transfer steps to methanol in a high production rate. Gang et al. [121] used MOFs to obtain Co single-atom catalyst with four co-ordinates N (Co-N) and N/C on the N-incorporated porous carbon. XAFs results show that for binding N to single atom Co, the coordination number was dependent on pyrolysis temperature. Their findings show that the Co atom attached to four N in N-incorporated porous carbon (Co-N$_4$) exhibit a Faradaic efficiency of about 82% with a current density of $-15.8$ mAcm$^{-2}$ for electrochemical CO$_2$ conversion to CO and was stable for 10 h. The mechanistic studies show that the Co-N$_4$ active centers are promoted by the binding power of CO$_2$, which facilitates the CO$_2$ activation and is responsible for high-performance CO$_2$ reduction.

![Figure 3](image-url)

**Figure 3.** Scheme for the single-step synthesis of PO-5 nm Co/SL-NG (a–d). Linear-sweep voltammograms of SL-NG catalyst, (e) PO-5 nm Co catalyst and (f) 30.87 wt% PO-5 nm Co/SL-NG catalyst in saturated CO$_2$ (red-line) and saturated-N$_2$ (blue-line) 0.1 mol dm$^{-3}$ NaHCO$_3$ electrolyte and the mechanism of CH$_3$OH production (g). Reproduced from [120], with permission from American Chemical Society, 2018.
He et al. [122] investigated the use of a single metal atom supported on defective graphene as a catalyst for electrochemical CO$_2$ conversion. The work studied the reaction pathway to produce C$_1$, CO, HCHO, HCOOH, CH$_3$OH and CH$_4$ using the selected five transition metals (i.e., Ag, Co, Cu, Pt, and Pd). The work further reveals that the single-atom catalysts exhibit an entire enhancement in the rate-limiting potential to generate C$_1$-hydrocarbons. However, a distinctive variation in terms of their efficiency and CO$_2$ conversion selectivity was reported. These differences were correlated to their elemental behavior as a role of their group number in the periodic table for the CH$_4$ generation. Thus single-atom catalysts are potential catalysts to overcome the overpotential problem associated with the CO$_2$RR.

2.2. Multi-Metals Cobalt Catalysts for CO$_2$RR

Electrochemical CO$_2$RR produces various forms of products ranging from CO, formic acid, alcohols, methane, olefin, and hydrocarbon [123]. However, the selectivity of these products is highly dependent on the adsorption characteristics of the reactants on the electrode surface. Due to the associated problems of metal electrocatalyst, transition metal catalysts could solve the problems to some extent because of the overpotential and poisoning [124], as metal and mixed metal electro catalysis still attracted scientific attention [125,126]. Recently, multimetatallic compounds have been given more attention to reducing material cost and tuning the strength of intermediate electrochemical reaction of CO$_2$ reduction to achieve high selectivity [127]. Multi-metals Co and Fe electrocatalyst were investigated for CO$_2$-reduction by Abdinejad and coworkers [71,99]. Their research finding reveals that the introduction of amino substituent enhanced the electrolytic activity toward the CO$_2$ conversion through dual active sites. The mono-amino FeP reduces the CO$_2$ to CO at ambient temperature and pressure with significant turnover (TON). They further reported the reactivity and selectivity of amino compounds towards capture and electroreduction of CO$_2$ in both homogeneous and heterogeneous [128].

Singh et al. [129] studied a direct electrochemical conversion of CO$_2$ to valuable products, using non-noble bimetallic (Ag-Co) electrocatalysts. The role of the catalyst was investigated over the gas phase electrochemical CO$_2$ conversion. It was found that, although the preferred metals are individually selective for CO generation, their combination results in the CH$_4$ and C$_2$H$_4$ generation along with the CO. A maximum Faradaic efficiency of ~20% for CH$_4$ production at 2 V using Ag-Co was reported. The effect of the binding power of the product formation during the CO$_2$ reduction affects the applied potential, and chemisorption characteristics of the metal. Likewise, the product formation distribution which facilitates the C-C bond formation resulted in higher hydrocarbons.

The AFM images of multi-metals of Cu and Co nanoparticles (NPs) shown in Figure 4a–d have a homogeneous size ranging from 1.2–21 nm. The effect of these particle sizes was explored on CO$_2$RR with different Co and Cu loading (i.e., x = 50, 70, 90 for Cu$_x$Co$_{100-x}$ system) by Bernal et al. [130]. The entire current density of the CuCo NPs as a function of nanoparticles size at $-1.1$ V vs. RHE presented in Figure 4e shows that the small-sized NPs are more active (i.e., activity increases with increase NPs). The selectivity expressed in Figure 4f–h with a different nominal metal composition (Cu = 50%, 70% and 90%) shows an increase in H$_2$ production with a decrease in NP size. The excellent activity was attributed to the presence of under coordinated site.
2.3. Cobalt Oxides Catalysts for CO$_2$RR

Cobalt oxides have been used extensively in CO$_2$RR as active catalysts as well as support materials. Aljabour et al. [131] used nanofibrous Co$_3$O$_4$ for the production of CO and formic acid. The nanofiber electrode exhibits stability for 8 h and overall Faradaic efficiency of about 90% for CO at a geometric current density of ~0.5 mAcm$^{-2}$ on a flat surface shown in Figure 5.

Figure 4. AFM micrographs of Cu$_{50}$Co$_{50}$ NPs with different sizes supported on SiO$_2$/Si (111). The average NP size: (a) 2.7 nm (S2), (b) 5.2 nm (S3), (c) 11.6 nm (S4), (d) 20.7 nm (S5). (e) Current density as a function of the particles size of Cu$_x$Co$_{100-x}$ NPs. Faradaic selectivity as a function of the NP size: (f) bimetallic Cu$_{50}$Co$_{50}$ complex, (g) Cu$_{70}$Co$_{30}$ complex, (h) Cu$_{90}$Co$_{10}$ complex. The data were obtained after 1 h of CO$_2$RR at E = −1.1 V vs. RHE. Reproduced from [130], with permission from Elsevier, 2018.

Figure 5. Electroreduction of CO$_2$ via the nanofibrous Co$_3$O$_4$. (a) increase in the amount of CO gas and formate as a function of time at a regular electrolysis potential of −1560 mV vs. NHE, (b) the electrolysis voltage versus the faradaic efficiency, (c) the chronoamperometry results, (d) Cyclic voltammograms of the electrode nanofibers measured before and after the electrolysis at a scan rate of 30 mV s$^{-1}$. Reproduced from [131], with permission from Elsevier, 2018.
Gao and coworkers [132] proposed an atomic layer for transition-metal oxide to improve the conventional electrocatalysts that frequently suffer from low efficiency and weak durability. The catalyst offers an ultra-large fraction of the active sites, elevated electronic conductivity and fine structural stability. Atomic thickness (1.72 and 3.52 nm) endowed the Co3O4 with abundant active sites that ensured a large CO2 adsorption. The Co3O4 layer with a thickness of 1.72 nm displayed over 1.5 and 20-times superior electrocatalytic performance than the 3.51 nm-thick layer electrode. The 1.72 nm Co3O4 layer displayed formate Faradaic efficiency of >60% in 2 h. The Zn and Co3O4 on graphite-plate works as the cathode and anode, respectively in the presence of Na and K carbonate and bicarbonate electrolytes. Their finding shows that HCOOH was the selective resultant product under all the applied conditions. The highest efficiency was achieved with the bicarbonates, using the KHCO3 electrolyte at 1.5 V, maximum Faradaic efficiency for HCOOH (78.5% and 78.46%) were achieved after 5 and 10 min reaction time. Similarly, 50% and 64.7% efficiency for CO was observed with NaHCO3 electrolyte at 2.5 V after 5 and 10 min, respectively. Similarly, another study by the same authors [133] for electrochemical reduction CO2. The study was conducted using CO2 dissolved in 0.5 M KHCO3 electrolyte at diverse applied voltages (1.5–3.5 V) and at a time interval of 5–25 min. The CO2 was converted to various products (such as HCOOH, CH2O, CH3H2O, CH3COOH, CH2OH) and ethanol as the main product. The ethanol as the main product of CO2 reduction with maximum Faradaic efficiency of 76.31% and 96.15% at 1.5 and 2 V, respectively, was obtained in a 5 min reaction. Cheng et al. [134] incorporated metal-oxide nanoclusters such as FeOx, NiOx and CoOx into the iron phthalocyanine (MOx/FePc) supported on graphene as electrocatalysts. The catalysts displayed high activity and selectivity along with stability for electrochemical CO2 reduction. Their findings show that the excellent activity is due to the fact that the MOx/FePc catalysts undergo replacement of the metal-ion with the iron center of Pc, thereby producing an electrochemical substituted metal-Pc (i.e., e-MPc, M = Co and Ni) co-existing with the substituted FeOx NPs in the neighborhood of e-MPc. Guo et al. [135] introduced the concept of combining an H2 evolution reaction (HER) with the Cdots/C3N4 heterojunction, a CO2 reduction electrocatalyst to have a cheap, stable, efficient and selective route for excellent production of syngas. They utilized MoS2, Co3O4, Au and Pt as the HER components. The Co3O4-Cdots-C3N4 electrocatalyst was highly efficient and the produced syngas H2/CO ratio was tuned from 0.07:1 to 4:1. The catalyst was found to be excellent for syngas production as the only product for >100 h. Gao et al. investigated the roles of oxygen vacancies in CO2 electro reduction with an apparent atomic-level association between the oxygen and the CO2 electro-reduction. The studies constructed model oxygen vacancies confined in an atomic layer using oxygen-deficient cobalt oxide single-unit layers. It was shown that the existence of oxygen (II) vacancies lowered the rate-limiting activation barrier from 0.51–0.40 eV via the stabilized formate-anion (HCOO−) radical intermediates. This was confirmed via the reduced onset potential from 0.81–0.78 V and the declined Tafel slope from 48–37 mVdec−1. The vacancies riched cobalt oxide single unit cell layer displayed a current density of 2.7 mAcm−2 with formate selectivity of 85%, during the 40 h test. Aljabour et al. [131] studied the catalytic behavior of semi-conducting Co3O4 nanofibers catalyst for CO2 conversion to CO using 65% Faradaic efficiency. The studies demonstrated the use of Co electrocatalysts without using any additional metal by expanding the electrode network with Nano-fibrous interconnection. A polyacrylnitrile polymer template was used to fabricate highly ordered Co3O4 nanofibers electrode. The amount of the products formed were increased by increasing electrolysis time. It was observed that CO formation dominates the format production which is attributed to the low proton number in the electrolyte. It was found that the optimum limit for operating voltage, the utmost Faradaic efficiency for CO generation was achieved at −1560 mV vs. NHE. The nanofibrous
Co$_3$O$_4$ electrodes performed for 8 h at a current density of 0.5 mA/cm$^2$. Significant degradation of the nanofiber electrode was observed but still stable and operational.

The bimetallic cobalt oxide with other metals has also been explored for ECO$_2$RR. The tin (Sn) and cobalt oxide (Co$_3$O$_4$) electrocatalytic effect for reduction of CO$_2$ was investigated by Yadav and Purkait [136]. The process was performed by using Sn and Co$_3$O$_4$ as cathode and anode, respectively, in 0.5 M KHCO$_3$ and NaHCO$_3$ electrolyte solutions at various applied voltages ranges and times. Their findings show formic acid formation with high Faradaic efficiencies of ~74% and 93% for the CHO0OH product obtained from 20 and 5 min reactions at 1.5 and 2 V applied potential. A CO$_2$RR to formate with low overpotential utilizing the Co$_3$O$_4$-CeO$_2$/low graphitic carbon (LGC) catalyst with oxygen-vacancies was studied by Zhang et al. [137]. The studies reveal that the overpotential for CO$_2$RR to produce formate on the Co$_3$O$_4$-CeO$_2$/LGC electrocatalyst was ~0.31 V (vs. RHE) and the highest Faradaic efficiency of the format was 76.4% at ~0.75 V vs. RHE (~61 mAc$^{-2}$) with high stability (i.e., 45 h). The catalyst displayed the formate production rate of 1.6 mmolm$^{-2}$s$^{-1}$C$^{-1}$mg$^{-1}$. It was shown that the coupling of Co$_3$O$_4$ to CeO$_2$/LGC led to a high concentration of oxygen vacancies and is regarded to be a key in the enhanced performance and stable selectivity with inhibited H$_2$-evolution reaction. A beached Au@Co$_3$O$_4$ nanowire array (Au@Co$_3$O$_4$ NAs) obtained by immersion in HAuCl$_4$ solution with Co$_3$O$_4$ nanowires was studied by Zhang et al. [138]. The catalyst exhibited excellent electrochemical activity by generating syngas (H$_2$ and CO) via turning from 1:1–4:1 with controlling voltage. It also showed a better catalytic activity for the oxygen evolution reaction with an overpotential of 320 mV at 50 mAc$^{-2}$ current density and a small Tafel slope of 75 mVdec$^{-1}$ in 1 M KOH electrolyte. The electrochemical activity of Au@Co$_3$O$_4$ NAs was better than the Co$_3$O$_4$ NAs, which opens up a feasible approach for the design and construction of a bifunctional electro-catalyst for an overall reaction. A proto-type bifunctional Co$_3$S$_4$@Co$_3$O$_4$ core–shell octahedron heterojunction catalyst synthesized by Yan and coworkers [139] was used for electro-reduction of oxygen and CO with high activity. The bifunctional electrocatalyst was shown to consist of a p-type core Co$_3$O$_4$ and n-type shell Co$_3$S$_4$ with high electron density. The synergistic interaction between the Co$_3$S$_4$ and Co$_3$O$_4$ bi-catalyst reduced the activation energy for conversion of the intermediates and enabled the CO$_2$-reduction reaction at low potentials. Formate was the highly selective main product at high Faradaic efficiency of ~85%, accredited to the synergistic coupling effect of co-catalyst structure. The exceptional synergistic effect of the metallic Co and the encapsulated coordinately unsaturated CoO display high activity for clean production of CO under moderate conditions. A CO$_2$ conversion of ~19% was attained with N-incorporated defective CoO shell (Co@CoO-N) with an exceptional CO production rate of 96 mLmin$^{-1}$g$^{-1}$ at 523 K with 42,000 mLg$^{-1}$h$^{-1}$ GHSV. The reaction mechanism is also described in detail as shown in Figure 6. Briefly, the surface of the Co-S bond adsorbs CO$_2$ to generate CO$_2$•– intermediate. The Co$_3$O$_4$ favors water splitting to form H$^+$ and OH$^–$. Subsequently, the CO$_2$•– reacts with H$^+$ and e$^–$ to create the product.
2.4. Cobalt-Based Nitride Catalysts

Cobalt nitrdes have proved beneficial for CO$_2$RR because they offer more surface basesites of adsorption of CO$_2$ and the generation of more active sites [140–146]. Peng et al. reported the highly efficient CO$_2$RR cobalt nitride catalysts (700-Co$_{5.47}$N/C) in an aqueous electrolyte. For the synthesis of these cobalt nitride catalysts, impregnation and nitridation involving temperature-programmed reaction (TRP) were used. For the optimized electrocatalyst 700-Co$_{5.47}$N/C, the observed CO current density was 9.78 mA cm$^{-2}$ at −0.7 V vs. RHE. The as-prepared electrocatalyst showed high Faradaic efficiency and good stability. Furthermore, tuning of the electrolysis potentials led to the CO/H$_2$ ratio adjustment from 3:1 to 3:2 [44]. In 2019, a robust synthesis strategy was adopted to synthesize the metal/nitrogen/carbon (MNC) catalysts with the presence of metal atoms as the atomically dispersed metal-N$_x$ moieties (wherein MN$_x$, M represents Mn, Co, Fe, Ni, and Cu metals) in N doped carbon using Zn MOF and metal salts. Jaouen et al. identified a volcano trend in MNC catalysts with MN$_x$, (M = Mn, Co, Fe, Ni, and Cu), providing an in-depth understanding of the activity and selectivity of atomically MN$_x$ with different metals for CO$_2$RR. MNC catalysts as promising candidates for CO$_2$RR were studied as model catalysts. Co was observed at the top of the volcano based on electrochemical potential. The experimental-operando X-ray absorption near edge structural spectroscopy was used for accurate modelling of active sites keeping the changes in the oxidation states of metals with change in potential. CoNC had no change in oxidation state with changing potential, and M$_2$ + N$_4$H$_2$O was identified as the most active center by computational studies. This work provided a base for the design and fabrication of cobalt-based MNC catalysts for CO$_2$RR to be used in the future [45]. The cobalt nitrogen functionalized materials are noteworthy catalysts for CO$_2$RR due to their high-performance activities. Metalloporphyrin and its derivatives have also been promising materials for catalytic activities [14]. Therefore, in 2019, Zhou et al. employed DFT calculations to study CO$_2$RR on Co-centered porphyrin and graphene with C, N and O as different coordinating atoms to further improve the activities. Through coordination engineering, the catalytic activities can be enhanced by the cobalt atom’s vacancy formation energy arising by substituting different coordinating atoms. Detailed electronic studies results showed that Co-O bonds lack π -bonding compared to the Co-N and Co-C bonds in the Co-centered structure, therefore, had potential for high catalytic activities. Hence, coordination engineering can be employed as an effective strategy for the enhancement of CO$_2$RR catalytic activities in cobalt nitrogen functionalized materials [147].
The CO$_2$RR performance of Co can be tuned via altering its coordination environment [121]. In 2020, Wang et al. utilized metal–organic layers (MOLs) as 2D analogous materials to MOFs and tuned the N-atom coordination number from 2 to 5 in the first sphere around the Co centers present on MOLs for optimization of electrocatalytic CO$_2$RR as shown in Figure 7. In these catalysts, Co centers supported on MOLs were chelated by the Bipyridine and terpyridine sites present on MOLs which prevented the equal distribution of ligands or other dimerization processes. Following phenylpyridine or bipyridine introduction to the chelated Co centers supported on MOLs led to the formation of CoN$_4$ and Co-N$_5$ centers. Therefore, in the as-prepared catalysts MOL-Co-N$_x$ (x = 2 to 5), bipyridine, phenylpyridine, and terpyridine ligands are the sources of different N atoms. In the case of MOL-Co-N$_3$, wrinkled ultrathin film-like structures are observed through TEM. Meanwhile HAADF and HRTEM depicted hexagonal structure patterns, which confirmed the Hf$_6$ SBUs present in MOL-Co-N$_3$. Among all the as-synthesized electrocatalysts, MOL-Co-N$_3$ displayed the highest CO$_2$RR performance with a significantly high CO Faradaic efficiency (FE-CO) of 99% at −0.5 V$_{RHE}$ [43]. The development of appropriate co-catalysts along with photocatalysts is a promising strategy for boosting CO$_2$ reduction. The use of co-catalyst has various advantages including lowered activation energy for CO$_2$, increased selectivity, promoted surface charge separation and enhanced stability. Therefore, keeping in view these advantages, metal nitrides can prove to be beneficial candidates for co-catalysts. Cobased nitrides can serve as an effective material to act as co-catalyst. Therefore, Liu et al., keeping in view the properties of metal nitrides, specifically cobalt nitrides, produced a novel cobalt nitride as a noble metal-free co-catalyst for enhancing the performance of BiOBr ultrathin nanosheets for effective CO$_2$ reduction. For the synthesis of Co$_2$N, a Co-based precursor was subjected to nitridation treatment and then Co$_2$N/BiOBr hybrid was formed. Exploration through TEM, aberration corrected-scanning TEM with high angle annular-dark-field imaging (HAADF-STEM) and atomic-resolved STEM image revealed the transparent morphology of BiOBr with an ultrathin thickness of 1.6 or 2.5 nm for 2 to 3 layers and lattice fringes of 0.277 nm corresponding to (110) plane. The morphology of Co$_2$N exhibits irregular structure with STEM images demonstrating the orthorhombic Co$_2$N. Meanwhile, coupling of BiOBr and Co$_2$N showed a well-defined nanosheet structure with uniform particle distribution. High selectivity CO formation rate was observed for Co$_2$N/BiOBr hybrid approximately 6 times higher than BiOBr with lowered activation energy and high stability leading to optimized CO$_2$ reduction activity [148].

Figure 7. Schematic representation of structure of Co-N$_x$ (x = 2 – 5) centers in the MOLs. Reproduced from [48], with permission from American Chemical Society, 2016.
For further insight into the enhancement of catalytic performances of TMNs for CO$_2$ RR, theoretical studies were presented for a clear understanding. Recently, Karamad et al. evaluated the catalytic activity and stability of various TMNs and their hetero-doped structures for CORR through high-throughput density functional theory (DFT). The results presented that various TMNs can activate the CORR but have electrochemical stability problems, including the competitive H$_2$ reaction. Therefore, only a few TMNs were found to be stable and active electrocatalysts [149]. The above discussion highlights the importance of cobalt nitrides for enhanced CO$_2$RR. These research works presented efforts to optimize the activity and selectivity of CO$_2$RR by tuning the electronic structures, compositions, morphology, and coordination chemistry of cobalt nitrides using different precursors and synthesis strategies to eliminate the drawbacks to achieve excellent activity and stability for CO$_2$RR.

2.5. Cobalt-Based Complexes for CO$_2$RR

Transition metal complexes offer an advantage for CO$_2$RR due to fine-tuning the coordination sphere via altering the chelating surroundings vis-à-vis electronic and steric effects of the chelating agents. Such fine-tuning is not possible in solid-state transition metal catalysts. Metal complex-type catalysts are available in the literature, ranging from noble metals (Ir, Ru, Re, etc.) to none-noble coinage metals (Co, Ni, Fe, Cu, etc.) [150,151]. These metals provide a two-electron reduction pathway to form -COOH$_x$ using organic reaction media. The porphyrin ring is an efficient ligand among other ligands because of its peculiar stability and high photo-electrochemical traits. A variety of cobalt complexes have been investigated for CO$_2$RR with promising results, there is still a need to find and generate a low-valent intermediate with significantly lower potential.

Qiu Tian reported CO$_2$ reduction over Ni and Co macrocyclic metallic complexes. In their findings, the tetramethylated Ni(TMcyclen) complex exhibited the best Faraday efficiency for CO production, which was followed by dimethylated Ni(DMcyclen) complex, and the Ni(cyclen) had no catalytic effect on the reaction [152]. Wang et al. reported CO$_2$ electrochemical reduction for cobalt phthalocyanine complexes supported over carbon (CoPc@carbon). The phthalocyanine used one trimethyl ammonium side chain and three tert-butyl moieties on the phthalocyanine macrocycle. They obtained a high current density of 165 mA.cm$^{-2}$ for CO against a potential of 0.92 V vs. RHE as shown in Figure 8. There highest CO selectivity was 99%, and stability for around 3 hr. the CoPc@carbon complexes were investigated using XANES spectra, which revealed the typical features of Co(II) phthalocyanine complexes [65]. Ogawa et al. reported CO$_2$ reduction over cobalt monoanionicbipyricorrole (Co(II)BIPC) complex and reported less overpotential. The crystal structure of Co(II)BIPC was determined by crystallography. They did cyclic voltammetry in DMF, which revealed two reversible peaks, i.e., E1/2 at $-0.87$ V and $-1.75$ V. they further corroborated that the first reduction even at $-0.87$ V is due to the Co(II)BIPC conversion to Co(II)BIPC. They conducted CO$_2$-to-CO electrocatalytic reactions under the CO$_2$ atmosphere, with emphasis on reducing the overpotential needed for the reaction. There Faraday efficiency was 75% at the overpotential of 0.35 V [69]. Roy et al. reported CO$_2$ reduction over cobalt phospho complexes [CpCo(PR2NR′2)2I] having diphosphine ligands and pendant amine moieties. The diphosphine and pendent amine residues were claimed to provide the necessary proton relay redox system for CRR. They claimed over 90% selectivity for formic acid at 0.5–0.7 V overpotential in DMF. They found that the Co complexes having the highest basic amine and the most electron-donating diphosphine moieties showed the best catalytic properties, i.e., TOF > 1000 s$^{-1}$. They corroborated their catalyst mechanism with the first-principle calculations employing TURBOMOLE, after geometry optimization with B3LYP functional. Their finding revealed the simplest possible way to convert CO$_2$ to formic acid, provided that the catalyst stability was properly addressed [64]. Nganga et al. [66] prepared a series of mono-, di-, and tri-β-oxo-substituted porphyrinoid-cobalt(II) complexes from porphyrin, for electrocatalytic conversion of CO$_2$. They reported that the monooxochlorin complex 2Co exhibit highest current than the
dimonooxochlorin 6Co, 7Co and dioxobacteriochlorin 4Co. In their report, they further reported the production of Co(II) complex–CH$_4$ via β-oxoporphyrinoid complexes, whereas CH$_4$ production was enhanced by β-oxoporphyrinoid complexes by 8 electron redox cycle. Xia et al. [67] reported on the dual active sites in cobalt phthalocyanine complexes for CO$_2$RR. They studied the reaction mechanism using synchrotron-based XAS and XPS analysis. They claimed that the catalyst showed dual active sites for the CO$_2$RR. In the first step, CO$_2$ gets attached to the N site on the cobalt phthalocyanine complex via protonating CO$_2$, to form a -COOH intermediate. In the second step, -COOH gets transferred to the Co central metal of the complex and is reduced to CO at the workable potential. By applying an optimum potential of 0.8 V, they reported over 95% CO production for a stable period of 5000 s. Liu et al. [153] used polymer coordination and encapsulation strategy, by using poly-4-vinylpyridine. Their catalytic system found >92% selectivity for CO over H$_2$ for 2 h, at $-1.25$ V vs. SCE and $-2.90$ mA.cm$^{-2}$ current density. The authors used kinetic isotope and proton inventory effect to explain the evident boost in the activity and selectivity of their polymer encapsulated cobalt phthalocyanine complexes. They reported that the proton relay mechanism is responsible for the higher selectivity towards CO, which suppressed the hydrogen evolution reactions. To boost the electrochemical properties of cobalt phthalocyanine complexes, Ma et al. [68] used polymer coordination and encapsulation strategy by using poly-4-vinylpyridine. Their catalytic system found >92% selectivity for CO over H$_2$ for 2 h, at $-1.25$ V vs. SCE and $-2.90$ mA.cm$^{-2}$ current density. The authors used kinetic isotope and proton inventory effect to explain the evident boost in the activity and selectivity of their polymer encapsulated cobalt phthalocyanine complexes. They reported that the proton relay mechanism is responsible for the higher selectivity towards CO, which suppressed the hydrogen evolution reactions. Jin et al. [154] studied the mechanism of the CO$_2$RR by cobalt Porphyrins towards CO, Formic acid, and methane. They report a density functional theory (DFT) study as shown in Figure 9. According to this finding that CO$_2^-$ anion the key intermediate, was formed when cobalt exists in the Co$^1$ oxidation state in cobalt porphyrins complexes. The CO generator is a major product during a decoupled proton-electron transfer. Methane has the lowest Faradic efficiency via subsequent CO conversion by the concerted proton-coupled electron-transfer reactions. Similarly, the formic acid product was minor through a [Co(P)-(OCHO)] intermediate.
Figure 8. Controlled potential electrolysis and CoPc2 film characterization. (a) Current density and selectivity for CO production as a function of the potential and (b) bulk electrolysis at a fixed potential ($E = -0.72$ V vs. RHE) for CoPc2@carbon black deposited onto a carbon paper as cathodic material, in 1 M KOH. c Co K-edge XANES profiles of CoPc2 (black dots) and CoPc2@carbon black before (blue) and after electrolysis ($E = -0.72$ V vs. RHE) (red) in 1 M KOH solution. Reproduced from [65], with permission from Nature Publishing Group, 2019.

Figure 9. Mechanism of the electrochemical CO$_2$ reduction catalyzed via the Co-Porphyrins. Reproduced from [154], with permission from Chemical Society, 2016.
2.6. Cobalt Porphyrin for CO$_2$RR

In recent years, porphyrin-based metal complexes have been significantly explored for CO$_2$ reduction [155]. This section keeps separately due to its broad research because porphyrin-ring offers high electron transfer activity, thus requiring relatively lower overpotential with high CO selectivity in the CO$_2$ reduction reactions. Additionally, researchers have made significant progress in porphyrin-based electrocatalysts anchored on potential host materials in terms of catalyst stability. Immobilized cobalt porphyrins have been reported for high faraday efficiency towards CO with lower overpotential. First principle calculations have also played a pivotal part in explaining the electronic structures of the metal-porphyrin catalytic systems for CO$_2$ reduction [156]. Shen et al. [70] immobilized cobalt protoporphyrins on pyrolytic graphite in aqueous media, and tested them for CO$_2$ reduction. The authors underpinned the pH stability of cobalt porphyrin electrocatalyst, saying that optimization of pH plays a crucial role in triggering the CO$_2$ reduction reaction. Their study claimed a >60% Faraday efficiency towards CO and >2.5% towards CH$_4$ was reported at a potential of $-0.6$ V vs. RHE, under acidic conditions. First principle calculations are important to understand the reaction pathways in the cobalt porphyrin electrocatalytic systems. In this regard, Leung et al. [157] performed the pioneering work by applying quantum chemistry and ab initio calculations in investigating the electrocatalytic effect of cobalt porphyrin complexes in the reductive decomposition of CO$_2$ in aqueous media. They used hybrid functionals alongside the dielectric continuum solvation methods, for determining the electron transfer mechanisms. They proposed a reductive mechanism that explained the CO$_2$ reduction at ambient to higher pH levels, which starts with one-electron transfer to the cobalt porphyrin complex [Co-porphyrin]$^-$, which then adds CO$_2$ to itself forming adjunct an [Co-porphyrin.CO$_2$]$^{2-}$. Upon protonation an intermediate [Co-porphyrin.COOH]$^-$ is produced, which upon relieving the OH$^-$ moiety, produces the product CO. The two key intermediates in this whole reaction cycle are [Co-porphyrin.CO$_2$]$_2$ and [Co-porphyrin.COOH]$^-$, due to the stronger interactions of CO$_2$ and water. Miyamoto and Asahi [158] reported on the enhanced CO$_2$ reduction to CO over cobalt porphyrin complexes in water based upon Koper’s mechanism. They combined their DFT calculations with the experimental results. Their work targeted the pH stability of their catalytic system, and reported that at pH = 3, a single proton shift from water occurs at $-0.8$ V vs. RHE. They said that water plays a vital role in the CO$_2$ reduction to CO, as their calculated redox potential of proton transfer matched that of the experimental results.

As a rule of thumb, the electron-withdrawing moieties on the electrocatalyst will facilitate the shifting of electrons to the catalyst core, but at the expense of the proton transfer step. Similarly, the electron-donating moieties facilitate the shifting of protons at the expense of the electron transfer step. Therefore, it is needed to find a middle ground between the electron-donating and electron-withdrawing moieties on the catalyst, to harness the CO$_2$ reduction reaction as per our needs. In this regard, amino groups attached to the porphyrin ring may come useful because the -NH$_2$ species acts as an electron-donating moiety that reverses its role to the electron-withdrawing group upon protonation. Abdinejad et al. [71] prepared cobalt and iron porphyrin complexes, where the porphyrin ring had amino moieties as electron transfer boosters. The authors attached different amino moieties to the porphyrin ring and reported higher catalytic activity of their catalyst. In their findings, cobalt porphyrin complexes were suitable for hydrogen production, while iron porphyrins were the most suitable catalysts for CO production. The FE selectivities towards CO and H$_2$ for the cobalt porphyrin were 8% and 99%, respectively. Meanwhile, the iron porphyrin produced 49% CO and 50% H$_2$ in their aqueous electrochemical catalytic system (Table 1).

2.7. Cobalt-Based MOFs and COFs for CO$_2$RR

The reticular chemistry of the MOFs and COFs enable the use of tunable control of the catalytic system to convert the carbon dioxide to value-added products [159]. However, this tunable property is prohibited by poor electrical conductivities. This can only
be overcome by the suitable use of the metals such as cobalt, copper in the inorganic SBUs. Katherine A. Mirica reported the synthesis of conductive two-dimensional MOF made of metallophalocyanine (cobalt/nickel) ligands linked by copper nodes with high electrical conductivities for the conversion of CO$_2$ to CO. It was observed that TOF values range from 1.15 and 0.63 s$^{-1}$ for CoPc-Cu-NH and CoPc-Cu-O [160]. Christopher J. Chang reported COF synthesis containing cobalt porphyrin catalysts as building units and organic linkers bonded through imine linkage to make the COF for the aqueous electrochemical reduction of CO$_2$ to CO. The COF materials were deposited on porous, conductive carbon fabric. Incorporating tubular molecular units of the porphyrins within the extended COF structure gave an advantage in electrocatalytic reduction with exceptionally high activity and selectivity. Thus we find that with the increasing length of the linker from COF-366 to COF-367, the activity is increased with the TON up to 290,000 and TOF of 9400 h$^{-1}$ about 26-fold more than the normal cobalt complex with no degradation over 24 h [161]. Rong Xu immobilized cobalt oxide nanoparticles on MIL-101 for water oxidation with a TOF of 0.012 s$^{-1}$ [162]. Jinhong et al. prepared cobalt immobilized on a covalent triazine-based framework (CTF) as an efficient cocatalyst to reduce CO$_2$ under visible-light irradiation. The CTF helps in the CO$_2$ adsorption while the pore structure helps in the accommodation of CO$_2$ and electron mediator. It was observed that the production of CO increases 44-fold than the pristine CTF on the introduction of cobalt. The obtained CO from this catalyst was about 50 mol g$^{-1}$h$^{-1}$ [163]. Peidong Yang et al. prepared a cobalt porphyrin-based Aluminum MOF for the conversion of CO$_2$ to CO with the TON up to 1400. In situ analysis showed that the majority of the redox-accessible Co(II) is reduced to Co(I) during catalysis [164]. Xinyong Li prepared a novel Z-scheme heterojunction of Co$_3$O$_4$@CoFe$_2$O$_4$ hierarchical hollow double-shelled nanoboxes derived from ZIF-67 to give CH$_4$ and CO at a rate of 2.06 mol h$^{-1}$ and 72.2 mol h$^{-1}$ respectively [164]. Yaghi et al. [165] prepared a new anionic 3D metal–organic framework MOF-1992 containing Co phthalocyaninioctaol. It converts CO$_2$ to CO with the TON up to 5800 and TOF 0.20 s$^{-1}$ with a current density of −16.2 mA cm$^{-2}$ at −0.52. The electroactive coverage of the catalyst was estimated with the aid of the CV measurement (Figure 10), and it was found to be ~25% of the total catalyst loading. Zhang et al. [166] studied a novel mixed-metallic MOF [Ag$_4$Co$_2$(PYZ)PDC$_4$] which transformed into an Ag-doped Co$_4$ catalyst. The Ag/Co$_3$O$_4$ catalyst gives the highest selectivity for CO in 0.1 M KHCO$_3$ electrolyte (CO$_2$ saturation), up to ~45% Faradaic efficiency was reported. Compared to the Ag/Co$_3$O$_4$ electrode, the highest Faradaic efficiency for CO over the pure Co$_3$O$_4$ is 21.3% at 1.8 V (vs. SCE). Their findings show that the presence of Ag improves the efficiency of CO significantly and inhibits H$_2$ production for 10 h at −1.8 V (vs. SCE). Pan et al. [40] used cobalt MOF as a precursor to synthesized electrocatalysts on carbon as model catalysts for CO$_2$RR. The prepared Co electrocatalyst was compared with Fe MOF-based electrocatalysts. The MOFs-derived catalysts were more active than the bulk electrocatalysts for CO$_2$ reduction over hydrogen production reaction.
Table 1. Performance of cobalt-based electrocatalysts for Electrochemical CO₂ reduction.

| Cobalt Group | Electrocatalysts | Electrolytic Solution | Potential | Current Density (mA/cm²) | Main Product | Faradic Efficiency (%) | Stability (h) | Ref |
|--------------|------------------|------------------------|-----------|--------------------------|--------------|------------------------|---------------|-----|
| Single atom | Atomic cobalt layers | 0.1 M Na₂SO₄ | −0.85 V vs. SCE | 10 | COOH | 90 | 60 | [167] |
| | single-atom Co-Tpy-c | 0.5 M NaClO₄ | −0.7 to −1.0 V (vs RHE) | 46.6 | CO | 95 | 24 | [116] |
| | Co/SL-NG | 0.1 M NaHCO₃ | −0.9 V vs. SCE | 4 | CH₃OH | 71.4 | 10 | [120] |
| | CoO-N | 0.1 M KC̶O₃ | −0.8 V vs. RHE | 15.8 | CO | 82 | 10 | [121] |
| | S̶ingle atom Co-N₃ | 0.2 M NaHCO₃ | −0.75 V vs. RHE | 6.2 | CO | 90 | 10 | [43] |
| | Ag-Co | 0.5 M KC̶O₃ | −2 V vs. RHE | NA | CH₄ | −20 | NA | [130] |
| | Cu-Co | 0.1 M KC̶O₃ | −1.1 V vs. RHE | 30 | H₂ | 85 | NA | [128] |
| | Co₃O₄/Sn | 0.5 M KC̶O₃ | 2 V | NA | HCOOH | 92.6 | NA | [136] |
| | Co₃S₄@Co₃O₄ | 0.1 M Na₂SO₄ | −0.64 V vs. RHE | 10 | HCOOH | 85.3 | NA | [139] |
| | Cu-Co | 0.1 M KC̶O₃ | −1.1 V vs. RHE | 30 | H₂ | 85 | NA | [128] |
| | Co₃O₄/Sn | 0.5 M KC̶O₃ | 2 V | NA | HCOOH | 92.6 | NA | [136] |
| | Co₃S₄ single-unit-cell layer | 0.1 M KC̶O₃ | −0.87 V vs. SCE | 2.7 | COOH | >85 | 40 | [168] |
| | Ultrathin Co₃O₄ | 0.1 M KC̶O₃ | −0.88 V vs. SCE | 0.68 | COOH | 60 | 20 | [132] |
| | Co₃O₄ nanofibers | 0.1 M KC̶O₃ | −1.5 V vs. SCE | 10 | CO | 65 | 8 | [131] |
| | Co₃O₄ | 0.1 M KC̶O₃ | −0.88 V vs. SCE | 0.68 | HCOOH | 60 | 20 | [132] |
| | CoO anode | 0.5 M KC̶O₃ | 2 V | 4.4 | C₂H₅OH | 96.5 | NA | [133] |
| | FeO/Cox | 0.5 M KC̶O₃ | −0.55 V vs. RHE | 14.49 | CO | 80 | 10 | [134] |
| | MOL-Co-N | 1.0 M KC̶O₃ | −0.5 V vs. RHE | 18.8 | CO | 99 | 10 | [43] |
| | 700-Co₂,ε/N/C | 0.5 M NaHCO₃ | −0.7 V vs. RHE | 9.78 | CO | NA | 10 | [44] |
| | CoNC | 0.5 M KC̶O₃ | −0.6 V versus RHE | 4.5 | CO | 45% | NA | [45] |
| | Single site catalyst STPyP-Co | 0.5 M KC̶O₃ | −0.62 V vs. RHE | 6.5 | CO | 96 | 48 | [46] |
| | Atomically dispersed (Co-N₂) | 0.5 M KC̶O₃ | −0.63 V vs. RHE | 18.1 | CO | 94 | 60 | [47] |
| | 700-Co₂,ε/N/C | 0.5 M NaHCO₃ | −0.7 V vs. RHE | 9.78 | CO | NA | 10 | [44] |
| | Co Complexes | 0.1 M NBu₄BF₄ in DMSO+H₂O | −2 V vs. Fe + / | COOH | 90 | 1 | [64] |
| | Cobalt phthalocyanine @MWCNT | 1 M KOH | −0.92 V vs. RHE | 165 | CO | 99 | 3 | [65] |
| | Cobalt Phthalocyanine | 0.1 M KC̶O₃ | −0.8 vs. RHE | 3 | CO | 99 | 1.3 | [67] |
| | CoPc-PAVP | 0.5 M KC̶O₃ | −0.68 V vs. RHE | 30 | CO | >90 | 12 | [68] |
| | Co(II) bipyricorrole | 0.35 V vs. Fe | CO | 75 | 1 | [69] |
| | Cobalt protoporphyrin | 0.1 M HClO₄ | −0.6 V vs. RHE | 0.44 | CO | 60 | 1 | [70] |
| | Cobalt protoporphyrin | 0.1 M perchlorate | −0.6 V vs. RHE | CO | 60 | 1.3 | [70] |
| | Cobalt tetraphenylporphyrin-NH₃ (MOF) | 0.1 M NBu₄PF₆ | −2.42 V vs. Ag/AgCl | H₂ | 99 | 4 | [71] |
| | Cobalt protoporphyrin (COFs) | 0.5 M KC̶O₃ | −0.74 V vs. RHE | 17.3 | CO | 85 | 10 | [121] |
| | Cobalt porphyrin | 0.5 M KC̶O₃ | −0.67 V vs. RHE | 5 | CO | 90 | 24 | [161] |
| | Cobalt-porphyrin (COFs) | 0.5 M KC̶O₃ | −0.67 V vs. RHE | 5.5 | CO | 76 | 7 | [164] |
| | MOF-1992 | 0.1 M KC̶O₃ | −0.52 V vs. RHE | 16.5 | CO | 80 | 6 | [165] |
| | Ag/Co-MOF | 0.1 M KC̶O₃ | −1.8 V vs. SCE | 20 | CO | 45 | 10 | [166] |
Figure 10. (a) Single-crystal X-ray structure of MOF-1992 based on the Fe-trimers and Co-porphyrin (CoPc). Atoms color: C-black; O-red; N-green; Co-orange; Fe-blue polyhedra. Hydrogen atoms and the chlorido ligands are omitted. The anionic charge of $[\text{Fe}_6(\text{OH}_2)_4(\text{CoPc})_3]^{6-}$, MOF-1992, was balanced by the presence of $[\text{X}]^n$ counterions ($\text{X}$ represents $\text{Mg}^{2+}$ or $\text{Fe}^{3+}$). Electrochemical characterizations of the MOF-1992 (b) Cyclic voltammetry (CV) of the MOF-1992/CB (CB, carbon black). The vertical line display the potential of Co-Pc-semiquinolate (CoPc-SQ) 4-/CoPc-catecholate (CoPc-cat) 8-redox couple (c) CV of the MOF-1992/CB in a $\text{CO}_2$-saturated (black, pH = 6.8) and $\text{N}_2$-saturated (green, pH = 7.2) $\text{KHCO}_3$ solution. Reproduced from [165], with permission from American Chemical Society, 2019.

3. Summary and Outlook

Carbon dioxide mitigation by non-noble, earth-abundant and cost-efficient catalysts like cobalt is favored for the long run. Due to several structural characteristics like unsaturated d-orbitals, multivalency, high coordinating ability, it can form a variety of catalysts. In addition, these cobalt catalysts have moderate $\text{CO}_2$ adsorption, high surface area and availability of more active sites for $\text{CO}_2$RR. Similarly, the latest research on cobalt catalysts, focusing on exploration through experimental studies and theoretical studies and emphasizing design and fabrication of cobalt-based electrocatalysts for $\text{CO}_2$RR, were summarized. Thus, this review’s critical analysis and guidance will provide new insights to future research and best practices for $\text{CO}_2$RR.

The electrochemical reduction of $\text{CO}_2$ using single-atom catalysts to generate high-value products is an attractive means of addressing the effects of alarming $\text{CO}_2$ emissions and the associated problems. Appropriate and increasing successes recorded in this field will address the ever-presented societal demand for chemicals and fuels. There is a need to develop excellent catalyst chemistries for this reaction, and it is always required to tune the activity and selectivity of the process, especially for the increased complex chemistries,
such as in the oxides of cobalt. Determining their surface binding energies towards the CO and H₂ adsorption using density functional theory will be crucial for evaluating their activity and selectivity. The use of multi-metallic catalysts is very active for the direct electrochemical reduction of CO₂ into valuable hydrocarbons. This is very important from the point of view to generate fuels from the CO₂. The formation of the hydrocarbons resulted from the alteration of binding energies and modified chemisorption properties of the involved catalyst metal. This is usually helpful in the development of a more effective and selective electro-catalyst. Cobalt complexes have great electronic conductivity and high Faradic efficiency. The porphyrin ring is an efficient complex ligand among several ligands because of its peculiar stability and high photo-electrochemical traits. A variety of cobalt complexes have been investigated for CO₂RR with good current density and Faradic efficiency but there is still a need to generate low-valent intermediate with significantly low overpotential. MOFs and COFs showed promising results for CO₂RR. However, their product Faradic efficiency is limited to CO and COOH only. This further enhancement in reaction product to higher alkanes is needed.

Co single-atom catalysts which are obtained from the pyrolysis of cobalt-containing organometallic complexes, polymer, MOF or by the loading of cobalt precursor onto the support, were revealed as promising catalysts for the CO₂RR. The single uniform atom leads to strong binding with the CO₂ resulting in an efficient reduction reaction with high Faradic efficiency toward CO formation. One of the few studies that showed the conversion of CO₂ to MeOH uses partially oxidized 5 nm cobalt nanoparticles dispersed on single layer nitrogen-depend graphene catalyst (PO-5 nm Co/SL-NG) with Faradaic efficiency of ~71% and current density of 4mAcm⁻² at 0.9 V.

A number of cobalt oxides were tested for the CO₂RR, nanofibers, atomic layer oxide, Zn-Co₂O₃ and Co₂O₃-FePc revealed decent Faradic efficiency for CO and HCOO-. Several factors affect the CO₂RR performance, selectivity and stability, the atomic thickness, which provides large actives sites for the CO₂ adsorption. The presence of oxygen vacancies in Co increases the performance and selectivity toward HCOO- formation.

Different C1 and C2 products (with ethanol as the main product) were also investigated upon the use of Co₃O₄ as anode electrode with Faradic efficiency of 76.31% and 96.15% at 1.5 and 2 V respectively were obtained in 5 min reaction. Meanwhile, H₂/CO was formed in a ratio of 0.07:1 to 4:1 by using The Co₃O₄-CDots-C₃N₄ electrocatalyst. Several studies investigate the utilization of cobalt nitride-based electrocatalysts for CO₂RR. With the use of various synthesis strategies, the coordination environment and state of Co, N and O can be tuned, which significantly influences the reduction performance. Experimental and computational data showed M2 + N4-H₂O and Co-Nx (x = 2–5) are the most active center sites for CO₂ reduction reaction and exhibit excellent Faradic efficiency for CO formation. Moreover, Co-based nitrides can be considered as an efficient co-catalyst for the photoelectrochemical reduction of CO₂. Co₂N served as a co-catalyst for the photocatalyst BiOBr and a remarkable enhancement in the selectivity, lower activation energy and stability toward the CO formation.

Among different cobalt complexes, cobalt-based porphyrins have been wildly explored for CO₂RR. The mechanistic studies explain that upon reduction reaction, the electron is attracted to the metal center, followed by the attachment of CO₂ to the complex, to be protonated to form the intermediate (Co-porphyrin.COOH), to produce CO in the presence of the electrolyte (OH⁻). Additionally, the amine moiety in the porphyrins serves as an electron-donating group, which facilitates the electron transfer to the complex center. However, some cobalt porphyrins with amines groups showed selectivity toward H₂ production compared to iron complexes.

Despite several advancements, further improvements for recommendation are given below:

1. Mixed metal catalysts: The numbers of electrons involved in the ECO₂RR are 2,8,12,14 for the formation of CO, methane, ethylene, and ethane, respectively. Bi and trimetallic catalysts are required to allow the charge transfer for the desire products especially CO₂ towards higher hydrocarbons.
2. Complexes: The use of organometallic complexes is still needed to increase the conjugation of the materials to overcome the conductivity problem for CO\textsubscript{2}RR for products higher than the eight-electron system.

3. Nanostructured electrocatalysts: The use of nanostructured cobalt catalysts can be further improved to gain a high current and to provide a high density of active sites for CO\textsubscript{2}RR.

4. In situ/operando measurements: It is crucial to understand the catalyst’s active sites, reduction pathway, and the type of intermediates by operando techniques.

5. Simulation data: The CO\textsubscript{2} electro reduction can be combined with simulation electrocatalysts to predict the product efficiency. A better reaction is needed to predict the catalyst development for efficient CO\textsubscript{2}RR.

6. Cobalt sulfide and selenide: The composites of cobalt sulfide and selenide can be explored for electrochemical CO\textsubscript{2}RR.

7. CO\textsubscript{2} reduction under impurities: The post-combustion plant contains several impurities along with CO\textsubscript{2}. Thus CO\textsubscript{2}RR in the presence of impurities must be tested to revealed electrode activity and stability.

8. Mixed gases data: CO\textsubscript{2} in the air is present as a mixture with other gases. The practical application of this technology is required to reduce the CO\textsubscript{2} in mixed gases electrochemically.

9. Current density: Currently, cobalt-based materials used liquid electrolytes with bubbled CO\textsubscript{2} for reduction. However, this gives low current density. The gas diffusion cells can be introduced to overcome this solubility issue by the liquid electrolytes and to achieve high current densities (>100 mA).

10. Use of solid electrolytes: A solid-state electrolyte configuration might overcome the challenge of CO\textsubscript{2} solubility and low current density.

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**References**

1. Draper, A.M.; Weissburg, M.J. Impacts of Global Warming and Elevated CO\textsubscript{2} on Sensory Behavior in Predator-Prey Interactions: A Review and Synthesis. *Front. Ecol. Evol.* 2019, 7. [CrossRef]

2. Gao, F.-Y.; Bao, R.-C.; Gao, M.-R.; Yu, S.-H. Electrochemical CO\textsubscript{2}-to-CO conversion: Electrocatalysts, electrolytes, and electrolyzers. *J. Mater. Chem. A* 2020, 8, 15458–15478. [CrossRef]

3. Shah, S.S.; Cevik, E.; Aziz, M.A.; Qahtan, T.F.; Bozkurt, A.; Yamani, Z.H. Jute Sticks Derived and Commercially Available Activated Carbons for Symmetric Supercapacitors with Bio-electrolyte: A Comparative Study. *Synth. Met.* 2021, 277, 116765. [CrossRef] [PubMed]

4. Garba, M.D.; Usman, M.; Khan, S.; Shehzad, F.; Galadima, A.; Ehsan, M.F.; Ghanem, A.S.; Humayun, M. CO\textsubscript{2} towards fuels: A review of catalytic conversion of carbon dioxide to hydrocarbons. *J. Environ. Chem. Eng.* 2021, 9, 104756. [CrossRef]

5. Usman, M.; Helal, A.; Abdelnaby, M.M.; Alloush, A.M.; Zeama, M.; Yamani, Z.H. Trends and Prospects in UiO-66 Metal-Organic Framework for CO\textsubscript{2} Capture, Separation, and Conversion. *Chem. Rec.* 2021, 21, 1771–1791. [CrossRef] [PubMed]

6. Usman, M.; Helal, A. Zirconium Metal-Organic Framework and a Method of Capturing Carbon Dioxide. U.S. Patent 16/677,277, 13 May 2021.
33. Garba, M.D.; Jackson, S.D. *trans*-Hydrogenation of pentane and 1-hexyne over CrOx/Al2O3. *Chem. Res. Toxicol.* 2018, 31, 167–175. [CrossRef]

32. Ehsan, M.F.; Shafiq, M.; Hamid, S.; Shafiee, A.; Usman, M.; Khan, I.; Ashiq, M.N.; Arfan, M. Reactive oxygen species: New insights into superoxide anion mediated photomineralization of methylene blue. *Appl. Catal. B: Environ.* 2020, 262, 118105. [CrossRef]

31. Ehsan, M.F.; Fazal, A.; Hamid, S.; Arfan, M.; Khan, I.; Usman, M.; Shafiee, A.; Ashiq, M.N.; Alotaibi, M.A.; Alharthi, A.I.; Din, I.U. *Renew. Sustain. Energy Rev.* 2020, 114, 109602. [CrossRef]

30. Din, I.U.; Usman, M.; Khan, S.; Helal, A.; Alotaibi, M.A.; Alharthi, A.I.; Centi, G. Prospects for a green methanol thermo-catalytic process from CO2 by using MOFs based materials: A mini-review. *J. CO2 Util.* 2021, 43, 101361. [CrossRef]

29. Garba, M.D.; Galadima, A. Catalytic Hydrogenation of Hydrocarbons for Gasoline Production. *Nanomaterials* 2021, 11, 2029. [CrossRef]

28. Alharthi, A.I.; Din, I.U.; Alotaibi, M.A. Effect of the Cu/Ni Ratio on the Activity of Zeolite Based Cu–Ni Bimetallic Catalysts for Dibenzothiophene Hydrodesulfurization and Methanol Reforming Reactions over Pd Promoted Alumina based Catalysts. *J. Fuel Clean Fuels.* 2016, 58, 1802066. [CrossRef]

27. Din, I.U.; Alotaibi, M.A.; Alharthi, A.I. Green synthesis of methanol over zeolite based Cu nano-catalysts, effect of Mg promoter. *Renew. Sustain. Energy Rev.* 2016, 62, 4251–4258. [CrossRef]

26. Kan, T.; Sun, X.; Wang, H.; Muhammad, U.; Li, C.; Zhang, S. *Catal. Sci. Technol.* 2016, 58, 129–1311. [CrossRef]

25. Zhang, C.; Wang, Q.; Jia, Z.; Muhammad, U.; Qian, W.; Wei, F. Design of parallel cyclones based on stability analysis. *AIChE J.* 2016, 62, 4251–4258. [CrossRef]

24. Zhang, H.; Cao, Y.; Li, D.; Muhammad, U.; Li, C.; Zhang, S. Catalytic hydrorefining of tar to liquid fuel over multi-metals intermediates for a methanol-to-olefins process. *Catal. Sci. Technol.* 2012, 113–125. [CrossRef]

23. Wang, H.; Cao, Y.; Li, D.; Muhammad, U.; Li, C.; Li, Z.; Zhang, S. *Adv. Funct. Mater.* 2015, 25, 2563–2568. [CrossRef]

22. Usman, M.; Li, D.; Li, C.; Zhang, S. Highly selective and stable hydrogenation of heavy aromatic-naphthalene over transition metal phosphides. *Sci. China Chem.* 2015, 58, 738–746. [CrossRef]

21. Cai, D.; Wang, Q.; Jia, Z.; Ma, Y.; Cui, Y.; Muhammad, U.; Wang, Y.; Qian, W.; Wei, F. Equilibrium analysis of methylbenzene intermediares for a methanol-to-olefins process. *Catal. Sci. Technol.* 2016, 6, 1297–1301. [CrossRef]

20. Ma, Y.; Cai, D.; Li, Y.; Wang, N.; Muhammad, U.; Carlsson, A.; Tang, D.; Qian, W.; Wang, Y.; Su, D.; et al. The influence of straight pore blockage on the selectivity of methanol to aromatics in nanosized Zn/ZSM-5: An atomic Cs-corrected STEM analysis study. *RSC Adv.* 2016, 6, 74797–74801. [CrossRef]

19. Zhang, C.; Wang, Q.; Jia, Z.; Muhammad, U.; Qian, W.; Wei, F. *Model. Simul. Eng.* 2020, 33, 1299–1311. [CrossRef]

18. Ashraf, M.; Khan, I.; Usman, M.; Khan, A.; Shah, S.S.; Khan, A.Z.; Saeed, K.; Yaseen, M.; Ehsan, M.F.; Tahir, M.N.; et al. Hematite and Magnetite Nanostructures for Green and Sustainable Energy Harnessing and Environmental Pollution Control: A Review. *Chem. Res. Toxicol.* 2020, 33, 1299–1311. [CrossRef]

17. Usman, M.; Zhu, J.; Chuiyiang, K.; Arslan, M.T.; Khan, A.; Galadima, A.; Muraza, O.; Khan, I.; Helal, A.; Al-Maythalyona, B.A.; et al. Propene Adsorption-Chemisorption Behaviors on H-SAPO-34 Zeolite Catalysts at Different Temperatures. *Catalysts* 2019, 9, 919. [CrossRef]

16. Arslan, M.T.; Qureshi, B.A.; Gilani, S.Z.A.; Cai, D.; Ma, Y.; Usman, M.; Chen, X.; Wang, Y.; Wei, F. Single-Step Conversion of H2-Deficient Syngas into High Yield of Tetramethylbenzene. *ACS Catal.* 2019, 9, 2203–2212. [CrossRef]

15. Zhu, J.; Li, Y.; Muhammad, U.; Wang, D.; Wang, Y. Effect of alkene co-feed on the MTO reactions over SAPO-34. *Chem. Eng. J.* 2017, 316, 187–195. [CrossRef]

14. Din, I.U.; Usman, M.; Khan, S.; Helal, A.; Alotaibi, M.A.; Alharthi, A.I.; Centi, G. *Small Methods* 2020, 4, 62, 101314. [CrossRef]

13. Zheng, T.T.; Jiang, K.; Wu, H.T. Recent Advances in Electrochemical CO2-to-CO Conversion on Heterogeneous Catalysts. *Adv. Mater.* 2018, 30, 1802066. [CrossRef]

12. Cheng, Y.; Yang, S.Z.; Jiang, S.P.; Wang, S.Y. *Small Methods* 2020, 4, 62, 101314. [CrossRef]

11. Khan, S.; Khulief, Y.A.; Al-Shuhail, A. The effect of injection well arrangement on injection into carbonate petroleum reservoir. *Appl. Petrochem. Res.* 2019, 9, 113–125. [CrossRef]
34. Garba, M.D.; Jackson, S.D. Catalytic upgrading of refinery cracked products by trans-hydrogenation: A review. Appl. Petrochem. Res. 2017, 7, 1–8. [CrossRef]

35. Akbar Jan, F.; Wajidullah; Ullah, R.; Ullah, N.; Salman; Usman, M. Exploring the environmental and potential therapeutic applications of Myrtus communis L. assisted synthesized zinc oxide (ZnO) and iron doped zinc oxide (Fe-ZnO) nanoparticles. J. Saudi Chem. Soc. 2021, 25. [CrossRef]

36. Jan, F.A.; Shah, U.; Saleem, M.; Ullah, R.; Ullah, N.; Usman, M.; Hameed, S. Photo catalytic degradation of xylene cyanol FF dye using synthesized bismuth-doped zinc oxide nanocatalyst. Biochem. Commun. 2021, 53, 83–90.

37. Medina, O.E.; Gallego, J.; Acevedo, S.; Riazi, M.; Ocampo-Pérez, R.; Cortés, F.B.; Franco, C.A. Catalytic Conversion of n-C7 Asphaltenes and Resins II into Hydrogen Using CeO2-Based Nanocatalysts. Nanomaterials 2021, 11, 1301. [CrossRef] [PubMed]

38. Li, J.; Prslja, P.; Shinagawa, T.; Martin Fernandez, A.J.; Krumeich, F.; Artyushkova, K.; Atanassov, P.; Zitolo, A.; Zhou, Y.; Pan, F.P.; Zhang, H.G.; Liu, K.X.; Cullen, D.; More, K.; Wang, M.Y.; Feng, Z.X.; Wang, G.F.; Wu, G.; Li, Y. Unveiling Active Sites of

39. Zedan, A.F.; Gaber, S.; AlJaber, A.S.; Polychronopoulou, K. CO Oxidation at Near-Ambient Temperatures over TiO2-Supported Pd-Cu Catalysts: Promoting Effect of Pd-Cu Nano-interface and TiO2 Morphology. Nanomaterials 2021, 11, 1675. [CrossRef] [PubMed]

40. Pan, F.P.; Zhang, H.G.; Liu, K.X.; Cullen, D.; More, K.; Wang, M.Y.; Feng, Z.X.; Wang, G.F.; Wu, G.; Li, Y. Unveiling Active Sites of CO2 Reduction on Nitrogen-Coordinated and Atomically Dispersed Iron and Cobalt Catalysts. ACS Catal. 2018, 8, 3116–3122.

41. Orudzhev, F.; Ramazanov, S.; Sobola, D.; Isaev, A.; Wang, C.; Magomedova, A.; Kadiev, M.; Kaviyarasu, K. Atomic Layer Deposition of Mixed-Layered Aurivillius Phase on TiO2 Nanotubes: Synthesis, Characterization and Photoelectrocatalytic Properties. Nanomaterials 2020, 10, 2183. [CrossRef]

42. Garba, M.D.; Jackson, S.D. Transhydrosgenation of pentane with 1,5- and 2,4-hexadiene over CrOx/Al2O3. Appl. Petrochem. Res. 2021, 11, 79–88. [CrossRef]

43. Guo, Y.; Wang, Y.C.; Shen, Y.; Cai, Z.Y.; Li, Z.; Liu, J.; Chen, J.W.; Xiao, C.; Liu, H.C.; Lin, W.B.; et al. Tunable Cobalt-Polypyridyl Catalysts Supported on Metal-Organic Layers for Electrochemical CO2 Reduction at Low Overpotentials. J. Am. Chem. Soc. 2020, 142, 21493–21501. [CrossRef]

44. Chen, M.; Peng-fei, H.; Peng, K. Electrocatalytic Reduction of Carbon Dioxide to Carbon Monoxide using Cobalt Nitride. J. Appl. Electrochem. 2019, 25, 467–476.

45. Li, J.; Pršlja, P.; Shinagawa, T.; Martin Fernandez, A.J.; Krumeich, F.; Artyushkova, K.; Atanassov, P.; Zitolo, A.; Zhou, Y.; Garcia-Muelas, R.; et al. Volcano Trend in Electrocatalytic CO2 Reduction Activity over Atomically Dispersed Metal Sites on Nitrogen-Doped Carbon. ACS Catal. 2019, 9, 10426–10439. [CrossRef]

46. Pan, Y.; Lin, R.; Chen, Y.; Li, S.; Zhu, W.; Cao, X.; Chen, W.; Wu, K.; Cheong, W.-C.; Wang, Y.; et al. Design of Single-Atom Co-N-5 Catalytic Site: A Robust Electro催化剂 for CO2 Reduction with Nearly 100% CO Selectivity and Remarkable Stability. J. Am. Chem. Soc. 2018, 140, 4218–4221. [CrossRef]

47. Wang, X.; Chen, Z.; Zhao, X.; Yao, T.; Chen, W.; You, R.; Zhao, C.; Wu, G.; Wang, J.; Huang, W.; et al. Regulation of Coordination Number over Single Co Sites: Triggering the Efficient Electroreduction of CO2. Angew. Chem. Int. Ed. 2018, 57, 1944–1948. [CrossRef]

48. Dongil, A.B. Recent progress on transition metal nitrides nanoparticles as heterogeneous catalysts. Nanomaterials 2019, 9, 1111. [CrossRef] [PubMed]

49. Humayun, M.; Ullah, H.; Tahir, A.A.; bin Mohd Yusoff, A.R.; Mat Teridi, M.A.; Nazeeeruddin, M.K.; Luo, W. An Overview of the Recent Progress in Polymeric Carbon Dioxide Based Photocatalysis. Chem. Rec. 2021. [CrossRef] [PubMed]

50. Liu, W.; Miao, Z.; Li, Z.; Wu, X.; Zhou, P.; Zhao, J.; Hao, S.; Wu, J.; Zou, S. Electroreduction of CO2 catalyzed by Co@N-C materials. J. CO2 Util. 2019, 32, 241–250. [CrossRef]

51. Miao, Z.; Liu, W.; Zhao, Y.; Wang, F.; Meng, J.; Liang, M.; Wu, X.; Zhao, J.; Zou, S.; Zou, J. Zn-Modified Co@N-C composites with adjusted particle size as catalysts for the efficient electroreduction of CO2. Catal. Sci. Technol. 2020, 10, 967–977. [CrossRef]

52. Adjo, S.O.; Ganiyu, S.A.; Usman, M.; Abdulazeez, I.; Alhooshani, K. Facile and efficient nitrogen modified porous carbon derived from sugarcane bagasse for CO2 capture: Experimental and DFT investigation of nitorgen atoms on carbon frameworks. Chem. Eng. J. 2020. 382. [CrossRef]

53. Usman, M.; Li, D.; Razzak, R.; Latif, U.; Muraza, O.; Yamani, Z.H.; Al-Maythalony, B.A.; Li, C.; Zhang, S. Poly aromatic hydrocarbon (naphthalene) conversion into value added chemical (tetralin): Activity and stability of MoP/AC catalyst. J. Environ. Chem. Eng. 2018, 6, 4525–4530. [CrossRef]

54. Din, I.U.; Shaharun, M.S.; Naeem, A.; Alothai, M.A.; Alharthi, A.; Nasir, Q. Effect of reaction conditions on the activity of novel carbon nanofiber-based Cu/ZrO2 catalysts for CO2 hydrogenation to methanol. Comptes Rendus. Chim. 2020, 23, 57–61. [CrossRef]

55. Din, I.U.; Shaharun, M.S.; Naeem, A.; Alothai, M.A.; Alharthi, A.; Nasir, Q. CO2 Conversion to Methanol over Novel Carbon Nanofiber-Based Cu/ZrO2 Catalysts—A Kinetics Study. Catalysts 2020, 10, 567. [CrossRef]

56. Usman, M.; Humayun, M.; Shah, S.S.; Ullah, H.; Tahir, A.A.; Khan, A.; Ullah, H. Bismuth-Graphene Nanohybrids: Synthesis, Reaction Mechanisms, and Photocatalytic Applications—A Review. Energies 2021, 14, 2281. [CrossRef]
57. Buliyaminu, I.A.; Aziz, M.A.; Shah, S.S.; Mohamedkhair, A.K.; Yamani, Z.H. Preparation of nano-CO$_2$O$_2$-coated Albizia procera-derived carbon by direct thermal decomposition method for electrochemical water oxidation. *Arab. J. Chem.* 2020, 13, 4785-4796. [CrossRef]

58. Shah, S.S.; Aziz, M.A.; Mohamedkhair, A.K.; Qasem, M.A.A.; Hakeem, A.S.; Nazal, M.K.; Yamani, Z.H. Preparation and characterization of manganese oxide nanoparticles-coated *Albizia procera* derived carbon for electrochemical water oxidation. *J. Mater. Sci. Mater. Electron.* 2019, 30, 16087–16098. [CrossRef]

59. Shah, S.S.; Alfasane, M.A.; Bakare, I.A.; Aziz, M.A.; Yamani, Z.H. Polyamine and heteroatoms–enriched carbon derived from *Pithophora polymorpha* composite for high performance supercapacitor. *J. Energy Storage* 2020, 30. [CrossRef]

60. Shah, S.S.; Qasem, M.A.A.; Berni, R.; Del Casino, C.; Iqbal, N.; Khan, U.A.; Waheab, A.; Raza, M.A.; Ashraf, S. Physico-chemical properties and toxicological effects on plant and algal models of carbon nanosheets from a nettle fibre clone. *Sci. Rep.* 2021, 11, 6945. [CrossRef]

61. Raziq, F.; Qu, Y.; Humayun, M.; Zada, A.; Yu, H.; Jing, L. Synthesis of SnO$_2$/B-P codoped g-C$_3$N$_4$ nanocomposites as efficient cocatalyst-free visible-light photocatalysts for CO$_2$ conversion and pollutant degradation. *Appl. Catal. B* 2017, 201, 486–494. [CrossRef]

62. Aziz, A.; Shah, S.S.; Kashem, A. Preparation and Utilization of Jute-Derived Carbon: A Short Review. *Chem. Rec.* 2020, 20, 1074–1098. [CrossRef]

63. Daiyan, R.; Chen, R.; Kumar, P.; Bedford, N.M.; Qu, J.; Cairney, J.M.; Lu, X.; Amal, R. Tunable Syngas Production through CO$_2$ Electroreduction on Cobalt–Carbon Electro catalyst. *ACS Appl. Mater. Interfaces* 2020, 12, 9307–9315. [CrossRef]

64. Roy, S.; Sharma, B.; Pécaut, J.; Simon, P.; Fontecave, M.; Tran, P.D.; Derat, E.; Artero, V. Molecular Cobalt Complexes with Pendant Amines for Selective Electrocatalytic Reduction of Carbon Dioxide to Formic Acid. *J. Am. Chem. Soc.* 2017, 139, 3685–3696. [CrossRef]

65. Wang, M.; Torbensen, K.; Salvatore, D.; Ren, S.; Joulié, D.; Dumoulin, F.; Mendoza, D.; Lassalle-Kaiser, B.; Içi, U.; Berlinguette, C.P.; et al. CO$_2$ electrochemical catalytic reduction with a highly active cobalt phthalocyanine. *Nat. Commun.* 2019, 10, 3602. [CrossRef] [PubMed]

66. Nganga, J.; Chaudhri, N.; Brückner, C.; Angeles-Boza, A.M. β-Oxochlorin cobalt(II) complexes catalyze the electrochemical reduction of CO$_2$. *Chem. Commun.* 2021, 57, 4396–4399. [CrossRef]

67. Xia, Y.; Kashtanov, S.; Yu, P.; Chang, L.-Y.; Feng, K.; Zhong, J.; Guo, J.; Sun, X. Identification of dual-active sites in cobalt phthalocyanine for electrochemical carbon dioxide reduction. *Nano Energy* 2020, 67. [CrossRef]

68. Ma, J.; Zhu, H.; Zheng, Y. Highly dispersed cobalt phthalocyanine on nitrogen-doped carbon towards electrocatalytic reduction of CO$_2$ to CO. *Ionics* 2021, 27, 2583–2590. [CrossRef]

69. Ogawa, A.; Oohora, K.; Gu, W.; Hayashi, T. Electrochemical CO$_2$ reduction by a cobalt bipyricorrole complex: Decrease of an overpotential value derived from monoanionic ligand character of the porphyrinoid species. *Chem. Commun.* 2019, 55, 493–496. [CrossRef]

70. Shen, J.; Kortlever, R.; Kas, R.; Birdja, YY.; Diaz-Morales, O.; Kwon, Y.; Ledezma-Yanez, I.; Schouten, K.J.P.; Mul, G.; Koper, M.T.M. Electro catalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilized cobalt protoporphyrin. *Nat. Commun.* 2015, 6, 1–8. [CrossRef]

71. Abdinejad, M.; Seifotikaldani, A.; Dao, C.; Sargent, E.H.; Zhang, X.-a.; Kraatz, H.B. Enhanced Electrochemical Reduction of CO$_2$ Catalyzed by Cobalt and Iron Amino Porphyrin Complexes. *ACS Appl. Energy Mater.* 2019, 2, 1330–1335. [CrossRef]

72. Humayun, M.; Zada, A.; Li, Z.; Xie, M.; Zhang, X.; Qu, Y.; Raziq, F.; Jing, L. Enhanced visible-light activities of porous BiFeO$_3$ by coupling with nanocrystalline TiO$_2$ and mechanism. *Appl. Catal. B* 2016, 180, 219–226. [CrossRef]

73. Yaqoob, L.; Noor, T.; Iqbal, N.; Nasir, H.; Sohail, M.; Zaman, N.; Usman, M. Nano composites of cobalt benzene Tricarboxylic acid MOF with rGO: An efficient and robust electrocatalyst for oxygen evolution reaction (OER). *Renew. Energy* 2020. [CrossRef]

74. Helal, A.; Usman, M.; Arafat, M.E.; Abdelnaby, M.M. Allyl functionalized UiO-66 metal-organic framework as a catalyst for the synthesis of cyclic carbonates by CO$_2$ cycloaddition. *J. Ind. Eng. Chem.* 2020, 89, 104–110. [CrossRef]

75. Helal, A. Fine Chemical Synthesis Using Metal–Organic Frameworks as Catalysts. In *Applications of Metal–Organic Frameworks and Their Derived Materials*; Scrivener Publishing LLC: Beverly, MA, USA, 2020; pp. 177–191.

76. Ahmad, A.; Iqbal, N.; Noor, T.; Hassan, A.; Khan, U.A.; Wahab, A.; Raza, M.A.; Ashraf, S. Cu-doped zeolite imidazole framework (ZIF-8) for effective electrocatalytic CO$_2$ reduction. *J. CO$_2$ Util.* 2021, 48. [CrossRef]

77. Mehek, R.; Iqbal, N.; Noor, T.; Nasir, H.; Mehmood, Y.; Ahmed, S. Novel Co-MOF/Graphene Oxide Electro catalyst for Methanol Oxidation. *Electrochim. Acta* 2017, 255, 195–204. [CrossRef]

78. Asghar, A.; Iqbal, N.; Noor, T.; Kariuki, B.M.; Kidwell, L.; Easun, T.L. Efficient electrochemical synthesis of a manganese-based metal-organic framework for H$_2$ and CO$_2$ uptake. *Green Chem.* 2021, 23, 1220–1227. [CrossRef]

79. Khan, J.; Iqbal, N.; Asghar, A.; Noor, T. Novel amine functionalized metal organic framework synthesis for enhanced carbon dioxide capture. *Mater. Res. Express* 2019, 6, 105539. [CrossRef]

80. Pi, W.; Humayun, M.; Li, Y.; Yuan, Y.; Cao, J.; Ali, S.; Wang, M.; Li, H.; Khan, A.; Zheng, Z.; et al. Properly aligned band structures in B-TiO$_2$/MIL53(Fe)/g-C$_3$N$_4$ ternary nanocomposite can drastically improve its photocatalytic activity for H$_2$ evolution: Investigations based on the experimental results. *Int. J. Hydrogen Energy* 2021, 46, 21912–21923. [CrossRef]

81. Israf Ud, D.; Qazi, N.; Mustapha, D.G.; Abdulrahman, I.A.; Mshari, A.A.; Muhammad, U. A Review of Preparation Methods for Heterogeneous Catalysts. *Mini Rev. Org. Chem.* 2021, 18, 1. [CrossRef]
82. Richard, L.A.; Moreau, P.; Rugmini, S.; Daly, F. Fischer-Tropsch performance correlated to catalyst structure: Trends in activity and stability for a silica-supported cobalt catalyst. *Appl. Catal. A Gen.* 2013, 464–465, 200–206. [CrossRef]

83. Fischer, N.; van Steen, E.; Claeyts, M. Structure sensitivity of the Fischer–Tropsch activity and selectivity on alumina supported cobalt catalysts. *J. Catal.* 2013, 299, 67–80. [CrossRef]

84. Li, C.; Tong, X.; Yu, P.; Du, W.; Wu, J.; Rao, H.; Wang, Z.M. Carbon dioxide photo/electroreduction with cobalt. *J. Mater. Chem. A* 2019, 7, 16622–16642. [CrossRef]

85. Wang, L.; Nitopi, S.A.; Bertheussen, E.; Orazov, M.; Morales-Guio, C.G.; Liu, X.; Higgins, D.C.; Chan, K.; Nørskov, J.K.; Hahn, C.; et al. Electrochemical carbon monoxide reduction on polycrystalline copper: Effects of potential, pressure, and pH on selectivity toward multicarbon and oxygenated products. *ACS Catal.* 2018, 8, 7445–7454. [CrossRef]

86. Guo, C.; Zhang, T.; Deng, X.; Liang, X.; Guo, W.; Lu, X.; Wu, C.M.L. Electrochemical CO₂ Reduction to C1 Products on Single Nickel/Cobalt/Iron-Doped Graphitic Carbon Nitride: A DFT Study. *ChemSusChem* 2019, 12, 5126–5132. [CrossRef] [PubMed]

87. Yaseen, M.; Humayun, M.; Khan, A.; Usman, M.; Ullah, H.; Tahir, A.A.; Ullah, H. Preparation, Functionalization, Modification, and Applications of Nanostructured Gold: A Critical Review. *Energies* 2021, 14, 1278. [CrossRef]

88. Han, J.; An, P.; Liu, S.; Zhang, X.; Wang, D.; Yuan, Y.; Guo, J.; Qu, X.; Hou, K.; Shi, L.; et al. Reordering d Orbital Energies of Single-Site Catalysts for CO₂ Electroreduction. *Adv. Mater.* 2017, 29, 20. [CrossRef]

89. Siahrostami, S.; Jiang, K.; Karamad, M.; Chan, K.; Wang, H.; Nørskov, J. Theoretical Investigations into Defected Graphene for Electrochemical Reduction of CO₂. *ACS Sustain. Chem. Eng.* 2017, 5, 11080–11085. [CrossRef]

90. Bhowsik, A.; Vegge, T.; Hansen, H.A. Descriptors and Thermodynamic Limitations of Electrocatalytic Carbon Dioxide Reduction on Rutile Oxide Surfaces. *ChemSusChem* 2016, 9, 3230–3243. [CrossRef] [PubMed]

91. Tayyebi, E.; Hussain, J.; Abghoui, Y.; Skulasou, E. Trends of Electrochemical CO₂ Reduction Reaction on Transition Metal Oxide Catalysts. *J. Phys. Chem. C* 2018, 122, 10078–10087. [CrossRef]

92. Kornienko, N.; Zhao, Y.B.; Kiley, C.S.; Zhu, C.H.; Kim, D.; Lin, S.; Chang, C.J.; Yaghi, O.M.; Yang, P. Metal-Organo Frameworks for Electrocatalytic Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* 2015, 137, 14129–14135. [CrossRef]

93. Hod, I.; Sampson, M.D.; Deria, P.; Kubiak, C.P.; Farha, O.K.; Hupp, J.T. Fe-Porphyrin-Based Metal-Organic Framework Films as High-Surface Concentration, Heterogeneous Catalysts for Electrochemical Reduction of CO₂. *ACS Catal.* 2015, 5, 6302–6309. [CrossRef]

94. Lei, Z.D.; Xue, Y.C.; Chen, W.Q.; Qiu, W.H.; Zhang, Y.; Horike, S.; Tang, L. MOFs-Based Heterogeneous Catalysts: New Opportunities for Energy-Related CO₂ Conversion. *Adv. Energy Mater.* 2018, 8, 31. [CrossRef]

95. Huang, J.F.; Buonsanti, R. Colloidal Nanocrystals as Heterogeneous Catalysts for Electrochemical CO₂ Conversions. *Chem. Mater.* 2019, 31, 13–25. [CrossRef]

96. Kinzel, N.W.; Werle, C.; Leitner, W. Transition Metal Complexes as Catalysts for the Electroconversion of CO₂: An Organometallic Perspective. *Angew. Chem. Int. Ed.* 2021, 60, 11628–11686. [CrossRef]

97. Abdinejad, M.; Dao, C.; Deng, B.; Dinic, F.; Voznyy, O.; Zhang, X.-A.; Kraatz, H.-B. Electrocatalytic Reduction of CO₂ to CO in Aqueous Solution Using Pyridine-Porphyrins Immobilized onto Carbon Nanotubes. *ACS Sustain. Chem. Eng.* 2020, 8, 9549–9557. [CrossRef]

98. Abdinejad, M.; Wilm, L.F.B.; Diehlmann, F.; Kraatz, H.B. Electrocatalytic CO₂ Reduction by Nickel Iridimazol-2-yldenaminoporphyrins in Both Heterogeneous and Homogeneous Molecular Systems. *ACS Sustain. Chem. Eng.* 2021, 9, 521–530. [CrossRef]

99. Abdinejad, M.; Hossain, M.N.; Kraatz, H.-B. Homogeneous and heterogeneous molecular catalysts for electrochemical reduction of carbon dioxide. *RSC Adv.* 2020, 10, 38013–38023. [CrossRef]

100. Abdinejad, M.; Santos da Silva, I.; Kraatz, H.B. Electrografting amines onto silver nanoparticle-modified electrodes for electroreduction of CO₂ at low overpotential. *Adv. Mater. A* 2021, 9, 1–8. [CrossRef]

101. Yang, P.; Wang, R.; Tao, H.; Zhang, Y.; Titirici, M.-M.; Wang, X.C. Cobalt Nitride Anchored on Nitrogen-Rich Carbons for Efficient Carbon Dioxide Reduction with Visible Light. *Catal. Sci. Technol.* 2021, 280, 119454. [CrossRef]

102. Nguyen, D.-T.; Nguyen, C.-C.; Do, T.-O. Rational one-step synthesis of cobalt clusters embedded-graphitic carbon nitriles for the efficient photocatalytic CO₂ reduction under ambient conditions. *J. Catal.* 2020, 392, 88–96. [CrossRef]

103. Zhu, M.; Yang, D.-T.; Ye, R.; Zeng, J.; Corbin, N.; Manthiram, A. Inductive and electrostatic effects on cobalt porphyrins for heterogeneous electrocatalytic carbon dioxide reduction. *Catal. Sci. Technol.* 2019, 9, 974–980. [CrossRef]

104. Qi, S.; Wu, D.; Dong, Y.; Liao, J.; Foster, C.W.; O’Dwyer, C.; Feng, Y.; Liu, C.; Ma, J. Cobalt-based electrode materials for sodium-ion batteries. *Chem. Eng. J.* 2019, 370, 185–207. [CrossRef]

105. Diercks, C.S.; Liu, Y.Z.; Cordova, K.E.; Yaghi, O.M. The role of reticular chemistry in the design of CO₂ reduction catalysts. *Nat. Mater.* 2018, 17, 943. [CrossRef]

106. Wang, Y.-R.; Huang, Q.; He, C.-T.; Chen, Y.; Liu, J.; Shen, F.-C.; Lan, Y.-Q. Oriented electron transmission in polyoxometalate-metalloporphyrin organic framework for highly selective electroreduction of CO₂. *Nat. Commun.* 2018, 9, 1–8. [CrossRef]

107. Lin, L.; Li, H.; Yan, C.; Li, H.; Si, R.; Li, M.; Xiao, J.; Wang, G.; Bao, X. Synergistic Catalysis over Iron-Nitrogen Sites Anchored with Cobalt Phthalocyanine for Efficient CO₂ Electroreduction. *Adv. Mater.* 2019, 31, 1903470. [CrossRef] [PubMed]
109. Li, T.T.; Mei, Y.; Li, H.W.; Qian, J.J.; Wu, M.; Zheng, Y.Q. Highly Selective and Active Electrochemical Reduction of CO\(_2\) to CO on a Polymeric Co(II) Phthalocyanine@Graphitic Carbon Nitride Nanosheet-Carbon Nanotube Composite. Inorg. Chem. 2020, 59, 14184–14192. [CrossRef] [PubMed]

110. Benson, E.E.; Kubiak, C.P.; Sathrum, A.J.; Smieja, J.M. Electrocatalytic and homogeneous approaches to conversion of CO\(_2\) to liquid fuels. Chem. Soc. Rev. 2009, 38, 89–99. [CrossRef] [PubMed]

111. Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. Chem. Soc. Rev. 2014, 43, 631–675. [CrossRef]

112. Kondratenko, E.V.; Mul, G.; Baltrusaitis, J.; Larrazábal, G.O.; Pérez-Ramírez, J. Status and perspectives of CO\(_2\) conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. Energy Environ. Sci. 2013, 6, 3112–3135. [CrossRef]

113. Boutin, E.; Robert, M. Molecular Electrochemical Reduction of CO\(_2\) beyond Two Electrons. Trends Chem. 2021, 3, 359–372. [CrossRef]

114. Tsiotslas, A.I.; Charisiou, N.D.; Yentekakis, I.V.; Goula, M.A. Bimetallic Ni-Based Catalysts for CO\(_2\) Methanation: A Review. Nanomaterials 2021, 11, 28.

115. Hui, S.; Shaigan, N.; Neburchilov, V.; Zhang, L.; Malek, K.; Eikerling, M.; Luna, P.D. Three-Dimensional Cathodes for Electrochemical Reduction of CO\(_2\): From Macro- to Nano-Engineering. Nanomaterials 2020, 10, 1884. [CrossRef] [PubMed]

116. Hou, P.; Song, W.; Wang, X.; Hu, Z.; Kang, P. Well-Defined Single-Atom Cobalt Catalyst for Electrocatalytic Flue Gas CO\(_2\) Reduction. Small 2020, 16, 2001896. [CrossRef]

117. Shi, L.; Ren, X.; Wang, Q.; Li, Y.; Ichihara, F.; Zhang, H.; Izumi, Y.; Ren, L.; Zhou, W.; Yang, Y.; et al. Stabilizing Atomically Dispersed Catalytic Sites on Tellurium Nanosheets with Strong Metal–Support Interaction Boosts Photocatalysis. Small 2020, 16, 2001896. [CrossRef]

118. Han, J.; Wang, D.; Du, Y.; Xi, S.; Hong, J.; Yin, S.; Chen, Z.; Zhou, T.; Xu, R. Metal–organic framework immobilized cobalt oxide nanoparticles for efficient photocatalytic water oxidation. J. Mater. Chem. A 2015, 3, 20607–20613. [CrossRef]

119. Sun, T.; Zhao, S.; Chen, W.; Zhai, D.; Dong, J.; Wang, Y.; Yang, S.; Han, A.; Gu, L.; Yu, R.; et al. Single-atomic cobalt sites embedded in hierarchically ordered porous nitrogen-doped carbon as a superior bifunctional electrocatalyst. Proc. Nat. Acad. Sci. USA 2018, 115, 12692–12697. [CrossRef] [PubMed]

120. Huang, J.; Guo, X.; Yue, G.; Hu, Q.; Wang, L. Boosting CH\(_3\)OH Production in Electrocatalytic CO\(_2\) Reduction over Partially Oxidized 5 nm Cobalt Nanoparticles Dispersed on Single-Layer Nitrogen-Doped Graphene. ACS Appl. Mater. Interfaces 2018, 10, 44403–44414. [CrossRef]

121. Geng, Z.; Cao, Y.; Chen, W.; Kong, X.; Liu, Y.; Yao, T.; Lin, Y. Regulating the coordination environment of Co single atoms for achieving efficient electrocatalytic activity in CO\(_2\) reduction. Appl. Catal. B 2019, 240, 234–240. [CrossRef]

122. He, H.; Jagvaral, Y. Electrochemical reduction of CO\(_2\) on graphene supported transition metals—Towards single atom catalysts. Phys. Chem. Chem. Phys. 2017, 19, 11436–11446. [CrossRef]

123. Hori, Y.; Kikuchi, K.; Suzuki, S. Production of CO and CH\(_4\) in electrochemical reduction of CO\(_2\) at metal electrodes in aqueous hydrogen carbonate solution. Chem. Lett. 1985, 14, 1695–1698. [CrossRef]

124. Inglis, J.L.; MacLean, B.J.; Pryce, M.T.; Vos, J.G. Electrocatalytic pathways towards sustainable fuel production from water and CO\(_2\). Coord. Chem. Rev. 2012, 256, 2571–2600. [CrossRef]

125. Singh, S.; Phukan, B.; Mukherjee, C.; Verma, A. Salen ligand complexes as electrocatalysts for direct electrochemical reduction of gaseous carbon dioxide to value added products. RSC Adv. 2015, 5, 3581–3589. [CrossRef]

126. Shaib, S.S.; Shaikh, M.N.; Khan, M.Y.; Alfasane, M.A.; Rahman, M.M.; Aziz, M.A. Present Status and Future Prospects of Jute in Nanotechnology: A Review. Chem. Rec. 2021, 21, 1631–1665. [CrossRef] [PubMed]

127. Peterson, A.A.; Norrskov, J.K. Activity Descriptors for CO\(_2\) Electroreduction to Methane on Transition-Metal Catalysts. J. Phys. Chem. Lett. 2012, 3, 251–258. [CrossRef]

128. Abdinejad, M.; Mirza, Z.; Zhang, X.-A.; Kraatz, H.-B. Enhanced Electrocatalytic Activity of Primary Amines for CO\(_2\) Reduction Using Copper Electrodes in Aqueous Solution. ACS Sustain. Chem. Eng. 2020, 8, 1715–1720. [CrossRef]

129. Singh, S.; Gautam, R.K.; Malik, K.; Verma, A. Ag-Co bimetallic catalyst for electrochemical reduction of CO\(_2\) to value added products. J. CO Util. 2017, 18, 139–146. [CrossRef]

130. Bernal, M.; Bagger, A.; Scholten, F.; Sinev, I.; Bergmann, A.; Ahmadi, M.; Rossmeisl, J.; Cuency, B.R. CO\(_2\) electroreduction on copper-cobalt nanoparticles: Size and composition effect. Nano Energy 2018, 53, 27–36. [CrossRef]

131. Aljabour, A.; Coskun, H.; Apaydın, D.H.; Ozel, F.; Hassel, A.W.; Stadler, P.; Sarici, N.S.; Kus, M. Nanofibrous cobalt oxide for electrocatalysis of CO\(_2\) reduction to carbon monoxide and formate in an acetonitrile-water electrolyte solution. Appl. Catal. B Environ. 2018, 229, 163–170. [CrossRef]

132. Xiao, J.; Jiao, X.; Sun, Z.; Zhang, W.; Sun, Y.; Wang, C.; Hu, Q.; Xu, Y.; Yang, F.; Yang, S.; et al. Ultrathin Co3O4 Layers Realizing Optimized CO\(_2\) Electroreduction to Formate. Angew. Chem. Int. Ed. 2016, 55, 698–702. [CrossRef] [PubMed]

133. Yadav, V.S.K.; Purkait, M.K. Electrochemical Studies for CO\(_2\) Reduction Using Synthesized Co\(_3\)O\(_4\) (Anode) and Cu\(_2\)O (Cathode) as Electrocatalysts. Energy Fuels 2015, 29, 6670–6677. [CrossRef]

134. Cheng, Y.; Veder, J.P.; Thomsen, L.; Zhao, S.; Saunders, M.; Demichelis, R.; Liu, C.; De Marco, R.; Jiang, S.P. Electrochemically substituted metal phthalocyanines, e-MPc (M = Co, Ni), as highly active and selective catalysts for CO\(_2\) reduction. J. Mater. Chem. A 2018, 6, 1370–1375. [CrossRef]
135. Guo, S.; Zhao, S.; Wu, X.; Li, H.; Zhou, Y.; Zhu, C.; Yang, N.; Jiang, X.; Gao, J.; Bai, L.; et al. A Co(3)O(4)-CDots-C(3)N(4) three component electrocatalyst design concept for efficient and tunable CO(2) reduction to syngas. Nat. Commun. 2017, 8, 1828. [CrossRef] [PubMed]

136. Yadav, V.K.; Purkait, M.K. Electrochemical reduction of CO2 to HCOOH on a synthesized Sn electrocatalyst using a Co3O4 anode. RSC Adv. 2015, 5, 68551–68557. [CrossRef]

137. Zhang, Q.; Du, J.; He, A.; Liu, Z.; Tao, C. Low overpotential electrochemical CO2 reduction to formate on Co3O4–CeO2/low graphitic carbon catalyst with oxygen vacancies. J. Solid State Chem. 2019, 279, 120946. [CrossRef]

138. Zhang, S.-Y.; Ma, J.-J.; Zhu, H.-L.; Zheng, Y.-Q. Self-supported beaded Au@Co3O4 nanowire arrays perform electrocatalytic CO2 reduction in water to syngas and water oxidation to O2. New J. Chem. 2020, 44, 11808–11816. [CrossRef]

139. Yan, Y.; Li, K.; Chen, X.; Yang, Y.; Lee, J.-M. Heterojunction-Assisted CoS3@Co3O4 Core–Shell Octahedrons for Supercapacitors and Both Oxygen and Carbon Dioxide Reduction Reactions. Small 2017, 13, 1701724. [CrossRef] [PubMed]

140. Zhu, X.W.; Ji, H.Y.; Yi, J.Y.; Yang, J.M.; She, X.J.; Ding, P.H.; Li, L.; Deng, J.J.; Qian, J.C.; Xu, H.; et al. A Specifically Exposed Cobalt Oxide/Carbon Nitride 2D Heterostructure for Carbon Dioxide Photoreduction. Ind. Eng. Chem. Res. 2018, 57, 17394–17400. [CrossRef]

141. Vinoth, S.; Ong, W.-J.; Pandikumar, A. Sulfur-doped graphitic carbon nitride incorporated bismuth oxychloride/Cobalt based type-II heterojunction as a highly stable material for photoelectrochemical water splitting. J. Colloid Interface Sci. 2021, 591, 85–95. [CrossRef] [PubMed]

142. Kumar, A.; Prajapati, P.K.; Aathira, M.S.; Bansiwal, A.; Boukherroub, R.; Jain, S.L. Highly improved photoreduction of carbon dioxide to methanol using cobalt phthalocyanine grafted to graphitic carbon nitride as photocatalyst under visible light irradiation. J. Colloid Interface Sci. 2019, 543, 201–213. [CrossRef]

143. Huang, P.; Huang, J.; Pantovich, S.A.; Carl, A.D.; Fenton, T.G.; Caputo, C.A.; Grimm, R.L.; Frenkel, A.I.; Li, G. Selective CO2 Reduction Catalyzed by Single Cobalt Sites on Carbon Nitride under Visible-Light Irradiation. J. Am. Chem. Soc. 2018, 140, 16042–16047. [CrossRef]

144. Fu, J.W.; Zhu, L.; Jiang, K.X.; Liu, K.; Wang, Z.H.; Qiu, X.Q.; Li, H.M.; Hu, J.H.; Pan, H.; Lu, Y.R.; et al. Activation of CO2 on graphitic carbon nitride supported single-atom cobalt sites. Chem. Eng. J. 2021, 415, 8. [CrossRef]

145. Roy, S.; Reisner, E. Visible-Light-Driven CO2 Reduction by Mesoporous Carbon Nitride Modified with Polymeric Cobalt Phthalocyanine. Angew. Chem. Int. Ed. 2019, 58, 12180–12184. [CrossRef]

146. Tian, S.; Chen, S.; Ren, X.; Hu, Y.; Hu, H.; Sun, J.; Bai, F. An efficient visible-light photocatalyst for CO2 reduction fabricated by cobalt porphyrin and graphitic carbon nitride via covalent bonding. Nano Res. 2020, 13, 2665–2672. [CrossRef]

147. Zhou, H.; Zou, X.; Wu, X.; Yang, X.; Li, J. Coordination Engineering in Cobalt-Nitrogen-Functionalized Materials for CO2 Reduction. J. Phys. Chem. Lett. 2019, 10, 6551–6557. [CrossRef] [PubMed]

148. Di, J.; Chen, C.; Zhu, C.; Song, P.; Duan, M.; Xiong, J.; Long, R.; Xu, M.; Kang, L.; Guo, S.J.N.E. Cobalt nitride as a novel cocatalyst to boost photocatalytic CO2 reduction. Nano Energy 2021, 79, 105429. [CrossRef]

149. Karamad, M.; Farimani, A.B.; Magar, R.; Siahrostami, S.; Gates, I.D. Heteroatom-Doped Transition Metal Nitrides for CO2 Electrochemical Reduction: A Density Functional Theory Screening Study. J. Phys. Chem. C 2020, 124, 26344–26351. [CrossRef]

150. Costentin, C.; Robert, M.; Savaéant, J.-M. Catalysis of the electrochemical reduction of carbon dioxide. Chem. Soc. Rev. 2013, 42, 2423–2436. [CrossRef] [PubMed]

151. Takeda, H.; Cometto, C.; Ishitani, O.; Robert, M. Electrons, Photons, Protons and Earth-Abundant Metal Complexes for Molecular Catalysis of CO2 Reduction. ACS Catal. 2017, 7, 70–88. [CrossRef]

152. Qiu, T. Electrochemical CO2 and O2 Reduction Using Nickel and Cobalt Macrocyclic Complexes; University of Delaware: Newark, DE, USA, 2016.

153. Liu, Y.; Mcrory, C.C.L. Modulating the mechanism of electrocatalytic CO2 reduction by cobalt phthalocyanine through polymer coordination and encapsulation. Nat. Commun. 2019, 10, 1683. [CrossRef] [PubMed]

154. Shen, J.; Kolb, M.J.; Götte, A.J.; Koper, M.T.M. DFT Study on the Mechanism of the Electrochemical Reduction of CO2 Catalyzed by Cobalt Porphyrins. J. Phys. Chem. C 2016, 120, 15714–15721. [CrossRef]

155. Manbeck, G.F.; Fujita, E. A review of iron and cobalt porphyrins, phthalocyanines and related complexes for electrochemical and photochemical reduction of carbon dioxide. J. Porphyr. Phthalocyanines 2015, 19, 45–64. [CrossRef]

156. Nielsen, I.M.B.; Leung, K. Cobalt—Porphyrin Catalyzed Electrochemical Reduction of Carbon Dioxide in Water. 1. A Density Functional Study of Intermediates. J. Phys. Chem. A 2010, 114, 10166–10173. [CrossRef]

157. Leung, K.; Nielsen, I.M.B.; Sai, N.; Medforth, C.; Shelnutt, J.A. Cobalt—Porphyrin Catalyzed Electrochemical Reduction of Carbon Dioxide in Water. 2. Mechanism from First Principles. J. Phys. Chem. A 2010, 114, 10174–10184. [CrossRef] [PubMed]

158. Miyamoto, K.; Asahi, R. Water Facilitated Electrochemical Reduction of CO2 on Cobalt-Porphyrin Catalysts. J. Phys. Chem. C 2019, 123, 9944–9948. [CrossRef]

159. Khan, N.A.; Humayun, M.; Usman, M.; Ghazi, Z.A.; Naeem, A.; Khan, A.; Khan, A.L.; Tahir, A.A.; Ullah, H. Structural Characteristics and Environmental Applications of Covalent Organic Frameworks. Energies 2021, 14, 2267. [CrossRef]

160. Meng, Z.; Luo, J.; Li, W.; Mirica, K.A. Hierarchical Tuning of the Performance of Electrochemical Carbon Dioxide Reduction Using Conductive Two-Dimensional Metallophthalocyanine Based Metal–Organic Frameworks. J. Am. Chem. Soc. 2020, 142, 21656–21669. [CrossRef]
161. Lin, S.; Diercks, C.S.; Zhang, Y.-B.; Kornienko, N.; Nichols, E.M.; Zhao, Y.; Paris, A.R.; Kim, D.; Yang, P.; Yaghi, O.M.; et al. Covalent organic frameworks comprising cobalt porphyrins for catalytic CO\textsubscript{2} reduction in water. *Science* **2015**, *349*, 1208. [CrossRef] [PubMed]

162. Ren, J.-T.; Zheng, Y.-L.; Yuan, K.; Zhou, L.; Wu, K.; Zhang, Y.-W. Self-templated synthesis of Co\textsubscript{3}O\textsubscript{4} hierarchical nanosheets from a metal–organic framework for efficient visible-light photocatalytic CO\textsubscript{2} reduction. *Nanoscale* **2020**, *12*, 755–762. [CrossRef] [PubMed]

163. Bi, J.; Xu, B.; Sun, L.; Huang, H.; Fang, S.; Li, L.; Wu, L. A Cobalt-Modified Covalent Triazine-Based Framework as an Efficient Cocatalyst for Visible-Light-Driven Photocatalytic CO\textsubscript{2} Reduction. *ChemPlusChem* **2019**, *84*, 1149–1154. [CrossRef] [PubMed]

164. Long, D.; Li, X.; Yin, Z.; Fan, S.; Wang, P.; Xu, F.; Wei, L.; Tadé, M.O.; Liu, S. Novel Co\textsubscript{3}O\textsubscript{4} @ CoFe\textsubscript{2}O\textsubscript{4} double-shelled nanoboxes derived from Metal–Organic Framework for CO\textsubscript{2} reduction. *J. Alloys Compd.* **2021**, *854*, 156942. [CrossRef]

165. Matheu, R.; Gutierrez-Puebla, E.; Monge, M.A.; Diercks, C.S.; Kang, J.; Prévot, M.S.; Pei, X.; Hanikel, N.; Zhang, B.; Yang, P.; et al. Three-Dimensional Phthalocyanine Metal-Catecholates for High Electrochemical Carbon Dioxide Reduction. *J. Am. Chem. Soc.* **2019**, *141*, 17081–17085. [CrossRef] [PubMed]

166. Zhang, S.-Y.; Yang, Y.-Y.; Zheng, Y.-Q.; Zhu, H.-L. Ag-doped Co\textsubscript{3}O\textsubscript{4} catalyst derived from heterometallic MOF for syngas production by electrocatalytic reduction of CO\textsubscript{2} in water. *J. Solid State Chem.* **2018**, *263*, 44–51. [CrossRef]

167. Gao, S.; Lin, Y.; Jiao, X.; Sun, Y.; Luo, Q.; Zhang, W.; Li, D.; Yang, J.; Xie, Y. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. *Nature* **2016**, *529*, 68. [CrossRef] [PubMed]

168. Gao, S.; Sun, Z.; Liu, W.; Jiao, X.; Zu, X.; Hu, Q.; Sun, Y.; Yao, T.; Zhang, W.; Wei, S.; et al. Atomic layer confined vacancies for atomic-level insights into carbon dioxide electroreduction. *Nat. Commun.* **2017**, *8*, 14503. [CrossRef] [PubMed]