Abstract: Processes for the conversion of CO\textsubscript{2} to valuable chemicals are highly desired as a result of the increasing CO\textsubscript{2} levels in the atmosphere and the subsequent elevating global temperature. However, CO\textsubscript{2} is thermodynamically and kinetically inert to transformation and, therefore, many efforts were made in the last few decades. Reformation/hydrogenation of CO\textsubscript{2} is widely used as a means to access valuable products such as acetic acids, CH\textsubscript{4}, CH\textsubscript{3}OH, and CO. The electrochemical reduction of CO\textsubscript{2} using hetero- and homogeneous catalysts recently attracted much attention. In particular, molecular CO\textsubscript{2} reduction catalysts were widely studied using transition-metal complexes modified with various ligands to understand the relationship between various catalytic properties and the coordination spheres above the metal centers. Concurrently, the coupling of CO\textsubscript{2} with various electrophiles under homogeneous conditions is also considered an important approach for recycling CO\textsubscript{2} as a renewable C-1 substrate in the chemical industry. This review summarizes some recent advances in the conversion of CO\textsubscript{2} into valuable chemicals with particular focus on the metal-catalyzed reductive conversion and functionalization of CO\textsubscript{2}.

Keywords: transition metals; catalysis; carbon dioxide

1. Introduction

Many efforts were devoted in the recent decades to utilizing CO\textsubscript{2} as a source for renewable energy and materials. Direct gas-phase reactions of CO\textsubscript{2} with other readily accessible small molecules, e.g., via the reformation with CH\textsubscript{4} to produce syngas (CO/H\textsubscript{2}) and acetic acid (Equations (1) and (2)), as well as hydrogenation to produce CH\textsubscript{4}, CH\textsubscript{3}OH, and CO (Equations (3)–(5)), were widely studied using mainly heterogeneous or supported metal catalysts [1–7]. Although these gaseous reactions convert CO\textsubscript{2} into useful products, the binary processes, which involve the reactions of CO\textsubscript{2} with explosive gases such as H\textsubscript{2} and CH\textsubscript{4}, are usually pressure-sensitive and, thus, require careful control over the reaction conditions. More handy chemical approaches via which diversified products can be derived directly from CO\textsubscript{2} are, therefore, highly desirable.

\[ \text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2; \Delta H^{\circ}_{298K} = +247.30 \text{ kJ/mol.} \] \hspace{1cm} (1)

\[ \text{CO}_2 + \text{CH}_4 \rightarrow \text{CH}_3\text{COOH}; \Delta H^{\circ}_{298K} = +8.62 \text{ kJ/mol.} \] \hspace{1cm} (2)

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}; \Delta H^{\circ}_{298K} = -165.00 \text{ kJ/mol.} \] \hspace{1cm} (3)

\[ \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}; \Delta H^{\circ}_{298K} = -90.70 \text{ kJ/mol.} \] \hspace{1cm} (4)

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}; \Delta H^{\circ}_{298K} = +41.19 \text{ kJ/mol.} \] \hspace{1cm} (5)

The catalytic reduction of CO\textsubscript{2} to CO, CH\textsubscript{3}OH, CH\textsubscript{4}, or higher hydrocarbons is considered an attractive approach for recycling CO\textsubscript{2}, whereby the energy from intermittent renewable sources is stored
at high density in the form of chemical bonds, mainly C–H. As one of the widely studied approaches, direct photochemical reduction of CO₂ using nano-sized hybrid heterogeneous photocatalysts, on which light is absorbed and charge separation takes place, occurs at the solid–liquid or solid–gas interface. The photogenerated charges are then transported to the surface, where the active sites mediate the catalytic reactions [8–14].

The electrochemical reduction of CO₂ on solid-state electrodes modified with nanocatalysts were recently shown to have good potential in yielding valuable products, e.g., acetate and ethylene, attracting much attention [15–17]; moreover, a large number of molecular metal catalysts were recently studied with the aim to reductively convert CO₂ into fuels using solar energy and electricity as the driving force [17–19]. The multiple accessible oxidation states of transition-metal complexes renders them suitable candidates for mediating multielectron redox processes such as CO₂ reduction, and the reactions are readily studied under homogeneous conditions using various conventional electrochemical and spectroscopic techniques. With the exception of the Lehn-type rhenium(I) tricarbonyl catalysts, i.e., Re(bpy)(CO)₃Cl (bpy = 2,2′-bipyridine, see Section 2.1), which are capable of acting as both electro- and photocatalysts of CO₂ reduction, the majority of the catalysts discussed herein work as stand-alone CO₂ reduction electrocatalysts, although the photochemical CO₂ reduction mediated by some of these catalysts was also reported in the presence of suitable photosensitizers and sacrificial donors [17–20]. On the other hand, chemical technologies or processes that utilize CO₂ as a renewable, non-toxic, and cost-efficient C-1 feedstock via coupling with various nucleophiles to produce more valuable chemicals, particularly more reduced and energetic products, also gained much attention [21–23]. However, given the wide variety of related processes, the discussion below focuses on transition-metal catalysts for the electroreduction and functionalization of CO.

2. Electrochemical Reduction of CO₂ on Molecular Transition-Metal Catalysts

The substantial energy barrier in activating CO₂ is reflected by the highly negative formal reduction potential of −2.14 V vs. saturated calomel electrode (SCE) for the one-electron reduction of CO₂ to CO₂⁻ [18,19,24], where a large overpotential is required for the rapid reduction of CO₂ to occur, largely as a result of the structural difference between the linear CO₂ and bent CO₂⁻ [19,20,24–26]. Alternatively, CO₂ can be reduced more easily via proton-assisted multiple electron transfer, which is more favorable thermodynamically [19,20,24–26]. Equations (6)–(11) show the typical processes for the reduction of CO₂ to different products and the corresponding reduction potentials vs. SCE [24]. These alternative pathways in turn affect the nature of products.

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HCO}_2\text{H}; -0.85 \text{ V (vs. SCE).} \quad (6) \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{CO} + \text{H}_2\text{O}; -0.77 \text{ V.} \quad (7) \\
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow \text{C} + 2\text{H}_2\text{O}; -0.44 \text{ V.} \quad (8) \\
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow \text{HCHO} + 2\text{H}_2\text{O}; -0.72 \text{ V.} \quad (9) \\
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{CH}_3\text{OH} + 2\text{H}_2\text{O}; -0.62 \text{ V.} \quad (10) \\
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}; -0.48 \text{ V.} \quad (11)
\end{align*}
\]

2.1. 4d and 5d Metal CO₂ Reduction Electro catalysts

A number of heavier transition-metal complexes were studied for their activity on CO₂ electroreduction. In particular, 4d and 5d transition-metal complexes bearing mainly bipyridyl and bidentate phosphine ligands were widely examined for their activity toward the two-electron reduction of CO₂. As these complexes are usually substitution labile and the derivatization of the related ligands are well reported, these heavier transition-metal CO₂ reduction catalysts are generally well characterized, and their catalytic properties are more readily tunable. Therefore, the corresponding
reaction mechanisms and intermediates are more widely reported. Examples of $4d$ and $5d$ metal catalysts are summarized in Tables 1 and 2.

### Table 1. $4d$ and $5d$ metal 2,2'-bipyridine (bpy) catalysts for two-electron CO$_2$ electroreduction.

| Catalyst                  | $E_{1/2}$ vs. SCE | TON | Solvent | Faradaic Efficiency | Reference |
|---------------------------|-------------------|-----|---------|---------------------|-----------|
| Re(bpy)(CO)$_3$Cl         | −1.49 V           | 300 | −       | −                   | [27]      |
| fac-Re(4,4'-OCH$_2$-bpy)(CO)$_3$X | −2.32 V $^c$ | 3.9 | −       | −                   | [28]      |
| cis-[Rh(bpy)$_2$(OTf)$_2$]$^+$ | −1.55 V $^a$ | −   | −       | 6.8−12.3            | [29]      |
| [Ru(bpy)$_2$(CO)]$^+$     | −1.50 V           | 10.7−25.5 | 7.8−10.1 | 2.1−21.7            | [29]      |
| cis-[Os(bpy)$_2$(CO)]$^+$ | −1.50 V           | 5.5  | −       | −                   | [30]      |
| cis-[Os(bpy)$_2$(CO)]$^+$ | −1.50 V           | 5.2  | −       | −                   | [30]      |
| trans-CI-Ru(bis(bpy))$_2$Cl$_2$ | −2.2 V $^c$  | 5.2  | −       | −                   | [31]      |

$^a$ Not detected; $^b$ not mentioned; $^c$ vs. Fc/Fc$^+$.  

A number of $4d$ and $5d$ 2,2'-bipyridine complexes (Re, Rh, Ru, and Os) catalyze the two-electron electroreduction of CO$_2$ to CO or formic acid/formate. For example, Re(bpy)(CO)$_3$Cl ($−1.49$ V vs. SCE, 98% Faradaic efficiency (FE) in dimethylformamide (DMF)/H$_2$O) catalyzes CO$_2$ reduction to produce CO [27]. A series of related Re complexes with different substituted bpy and labile ligands, $^{fac}$-Re(4,4'-R-bpy)(CO)$_3$X (bpy = 2,2'-bipyridine, R = OCH$_3$, CH$_3$, iBu, H, CN, CF$_3$; X = Cl, Br, bpy(OTf), or CH$_3$CN(OTf)) were studied for their electrocatalytic efficiency with and without addition of a proton source (PhOH, CH$_3$COOH, CF$_3$CH$_2$OH) [28]. The results showed that the catalytic activity and overpotential increase with the electron-donating ability of the bpy substituents and the addition of acid positively shifted the catalytic current response of Re(4bpy)(CO)$_3$Cl ($−170$ mV) [28]. Additionally, cis-[Rh(bpy)$_2$(Cl)$_2$]$^+$ (X = Cl or OTf) reduces CO$_2$ to formate ($−1.55$ V vs. SCE, 64% FE, turnover number (TON) = 6.8−12.3) [29]. A series of functionalized Re(I) tricarbonyl catalysts, [Re(bpyMeamins)][CO$_3$Cl]PF$_6$ (Scheme 1), bearing redox-active imidazolium groups in the secondary coordination sphere, were reported to demonstrate improved catalytic activities as compared to the reference Re(bpy)(CO)$_3$Cl catalyst such that the potentials of the reductive catalytic current were approximately 170 mV less negative, and the Faradaic efficiency for CO generation was increased by 19% [30]. Recently, a water-soluble rhenium(I) tricarbonyl electrocatalyst with two hydroxymethyl moieties, [Re(CH$_2$OH)$\cdot$OH$_2$]$^+$ (Scheme 1), was studied for CO$_2$ reduction in aqueous solutions. Controlled-potential electrolysis using the catalyst at $−1.1$ V vs. normal hydrogen electrode (NHE) in a pH 6.9 CO$_2$-saturated aqueous solution yielded CO and HCOOH at selectivities of 95% and 4%, respectively [31].

![Scheme 1. Structures of $[\text{Re(bpyMeamins)}]_{\text{CO}_3}\text{Cl}^+$ and $[\text{Re(CH}_2\text{OH)}\cdot\text{OH}_2]^+$ [30,31]; bpy—2,2'-bipyridine.](image-url)
Ru(bpy)$_2$(CO)X (X = CO or Cl) and [M(bpy)$_2$(CO)H]$^+$ (M = Os and Ru) reduce CO$_2$ to CO/H$_2$/HCOO$^-$ and CO, respectively [32,33]. Recently, trans-Cl-Ru(mesbpy)(CO)$_2$Cl$_2$ (mesbpy = 6,6'-dimesityl-2,2'-bipyridine) was reported to reduce CO$_2$ to CO and formate with turnover frequencies (TOF) = 1300 s$^{-1}$ [34]. Phosphine complexes of 4$d$ and 5$d$ transition metals such as Rh(dppe)$_2$Cl (dppe = 1,2-bis(diphenylphosphino)ethane) (−1.55 V vs. SCE, 42% FE) and (m-(triphos)$_2$-[Pd(CH$_3$CN)$_2$]$_2$(BF$_4$)$_4$) (triphos = bis(diphenylphosphinoethyl)phenylphosphine) reduce CO$_2$ to formate and CO (Table 2) [35–37].

Table 2. Polyphosphine metal catalysts for two-electron CO$_2$ electroreduction. dppe—1,2-bis(diphenylphosphino)ethane; triphos—bis(diphenylphosphinoethyl)phenylphosphine.

| Catalyst | TON | Solvent | Faradaic Efficiency | Reference |
|----------|-----|---------|---------------------|-----------|
| Rh(dppe)$_2$Cl | - | 1.58 | MeCN | 42% | [35] |
| [Pd(etpC)(DMF)](BF$_4$)$_2$ | 130 | - | 154 | DMF | 85% | [36] |
| (m-(triphos)$_2$-[Pd(CH$_3$CN)$_2$]$_2$(BF$_4$)$_4$ | 190 | - | - | DMF | 80% | [37] |

- Not mentioned.

2.2. 3d Metal CO$_2$ Reduction Electro catalysts

Although the 4$d$ and 5$d$ CO$_2$ reduction catalysts of bidentate ligands, especially bipyridyl ligands, attracted much attention, the relatively low abundance of these metals prompted the development of cost-efficient catalysts and, subsequently, the study of 3$d$ transition-metal catalysts for CO$_2$ reduction. Probably as a result of their better stability in the reduced state, a number of 3$d$ metal complexes bearing macrocyclic and tetradentate chelating ligands were investigated for activity toward CO$_2$ electroreduction. Cobalt, iron, and nickel tetraaza macrocyclic complexes were reported to catalyze the electrochemical reduction of CO$_2$. Eisenberg first reported the use of cobalt and nickel tetraaza macrocyclic complexes as electrocatalysts for CO$_2$ reduction (at −1.3 to −1.6 V vs. SCE) to CO or CO/H$_2$ mixture in aqueous acetonitrile at nearly quantitative FE (Scheme 2) [38]. Mechanistic studies for catalytic CO$_2$ reduction were also reported using Co complexes of similar ligands [39–42].

![Scheme 2. Structures of Co and Ni tetraaza macrocyclic complexes](https://example.com/scheme2.png)

[Ni(cyclam)]$^{2+}$ and other structurally related Ni complexes (Scheme 3) exhibit remarkable efficiency and selectivity for reduction of CO$_2$ to CO on a mercury electrode (at −0.86 V vs. SCE) in purely aqueous solution (pH 4–5) [43–45]. Product selectivity depends on the pH and potential at which the controlled potential electrolysis was performed [46,47]. Electrolysis of a CO$_2$ saturated solution (pH 4.1) containing [Ni(cyclam)]$^{2+}$ at −1.00 V vs. SHE (overpotential = 640 mV) on an Hg electrode yields CO almost quantitatively at 96% FE and a TON of 116 [43,44]. N-substituted Ni cyclams exhibit similar activity and produce CO at high FE of 84–92% at pH 5 and 550 mV overpotential. Formic acid is obtained similarly, with CO as the byproduct, using the dimeric ([Ni(cyclam)]$_2$)$^{4+}$ and related derivative (Scheme 3) at 75% and 68% FE, respectively, in DMF on an Hg electrode at −1.4 V vs. SCE (460 mV overpotential) [48].
The CO₂ reduction activity of CoII tetraazamacrocycle [Co(CR)]²⁺ (CR = 2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]-heptadeca-1(17),2,11,13,15-pentaene) was studied by Tinnemans et al. and Che et al. (Scheme 4) [49,50]. Electrocatalysis using the complex on a carbon electrode yields CO selectively at 20–30% FE in acetonitrile (overpotential = 940 mV). Peters et al. later reported an enhanced FE of 45% in the presence of 10 M H₂O. A related Fe pentaazamacrocycle [FeIII(LN₅)Cl]⁺ (Scheme 4) was recently reported by Lau and co-workers to catalyze the electroreduction of CO₂ to HCOOH in DMF at −1.25 V vs. SCE (310 mV overpotential) on a glassy carbon electrode, producing formic acid at 75% FE with a TOF of 0.12 s⁻¹ [51].

Iron(0) porphyrin complexes were widely studied for electrocatalytic reduction of CO₂ to CO by Savéant et al. and are among the most efficient homogeneous molecular catalysts in aprotic solvent (DMF and acetonitrile (can)) [52–55]. Fe(TPP) was found to selectively catalyze the reduction of CO₂ to CO at −1.8 V vs. SCE in DMF (Scheme 5, R = H) [56–59]. The catalysis is significantly enhanced by the presence of weak Brönsted acids (water, trifluoroethanol, and phenol), as well as Lewis acids. For example, electrolysis using Fe(TPP) at −1.46 V vs. SHE on a mercury pool electrode in DMF, with phenol as the added acid, yields CO between 100% and 94% at varied phenol concentrations (0.1 to 1 M). When 1-propanol (6.7 M) is added instead, formic acid (35% yield) and CO (60% yield) were obtained on a mercury pool at −1.7 V vs. SCE, along with minor byproducts such as H₂ and oxalate [59]. Fujita et al. later reported that iron(IV) and cobalt(III) corrole complexes similarly catalyze the reduction of CO₂ to CO at −1.7 V vs. SCE under homogeneous conditions (Scheme 5) [60,61].
Cobalt porphyrin (CoTPP) and phtalocyanine (CoPc) complexes were also found to be catalytically active in water on carbon electrodes film-coated with the complexes [24,62–66]. By using the Co(TPP) (Scheme 6) deposited on a carbon black gas-diffusion electrode, CO is produced at -0.76 V vs. SHE (overpotential = 230 mV) at 97% FE in a 0.5 M KHCO₃ solution under a high CO₂ pressure of 20 atm. Similarly, CO is produced in 80% FE at pH 4.6 with TOF = 140 h⁻¹ and TON = 1100 using cobalt chlorin (CoCh) deposited on carbon nanotubes (700 mV overpotential) [66]. Cobalt protoporphyrin (CoPP) deposited on pyrolytic graphite also catalyzes the CO₂-to-CO conversion at a low pH of 3 at 60% FE and 500 mV overpotential under 10 atm of CO₂, while 2.5% CH₄ was obtained when the pH was lowered to 1 [24].

The introduction of intramolecular phenolic protons at the ortho and ortho’ positions of Fe(TPP) was found to be effective in enhancing the efficiency of CO₂ electroreduction to CO and the catalyst durability (Scheme 7) [53,54]. The catalyst (FeTDMPP) operates at a lower overpotential (450 mV) compared with FeTPP (600 mV), while the substitution of a trimethylammonio group (Fe-p-TMA) not only increases the CO conversion efficiency and selectivity, but also catalyzes the reduction of CO₂ to methane [55,67,68].

Heterogeneous catalytic materials based on solid-support or supramolecular porphyrin catalysts of Co, Cu, and Fe for the reduction of CO₂ in aqueous solutions were explored. A catalytic electrode constructed from two-dimensional (2D) covalent organic frameworks (COFs) of cobalt tetraakis(4-aminophenyl)porphyrin (Co(TAP)) on porous conductive carbon fabric was found to demonstrate significantly improved (26-fold) catalytic activity for CO₂-to-CO conversion at an overpotential of −0.55 V (FE of 90%, TON up to 290,000, and initial TOF of 9400 h⁻¹) at pH 7 with respect to the molecular cobalt complex under the same condition [69]. A similar catalytic electrode was prepared by depositing a porous organic cage (Fe-PB), which bears six Fe(TPP) centers, onto a glassy carbon electrode coated with carbon nanotubes (CNTs/GCE) [70]. Both electrochemically active surface area (3.7 nmol EA-Fe·cm⁻² vs. 2.5 nmol EA-Fe·cm⁻²) and mass transport were increased.
for Fe-PB/CNTs/GCE with respect to the Fe(TPP)/CNTs/GCE containing an equivalent amount of Fe(TPP), resulting in an enhanced catalytic current response, CO/H₂ selectivity, and product turnover (TON = 55,250 after 24 h and TOF = 0.64 s⁻¹ vs. TON = 32,770 after 24 h and TOF = 0.38 s⁻¹) for controlled potential electrolysis at −0.63 V vs. RHE. Cu(II)-5,10,15,20-tetrakis(2,6-dihydroxyphenyl)porphyrin) Cu(TDMPP) deposited on a commercial porous polytetrafluoroethylene-treated carbon fiber paper reduces CO₂ to hydrocarbons (methane and ethane) at −0.976 V vs. RHE at 44% FE [71].

A number of 3d metal complexes (Co, Fe, and Ni) bearing tetradentate chelating ligands of N, C, and O donor atoms were reported to be active electrocatalysts for the selective reduction of CO₂ to CO. The N-heterocyclic carbene–isoquinoline complexes [Ni(Pbimiq1)]²⁺ ([Pbimiq1 = bis(3-(imidazolyl))isoquinolinyl)propane) (Scheme 8) were also reported to catalyze CO₂-to-CO electroreduction, yielding CO at an optimal FE of 90% (overpotential = 840 mV) on a glassy carbon electrode; however, the catalytic efficiency was found to decrease significantly upon prolonged electrolysis [72]. Co-azacalix[4][2,6]pyridine catalysts (Scheme 8) containing methyl- and allyl-substituted macrocyclic aminopyridine ligands were reported to selectively produce (optimal FE = 98%) CO in a CO₂-saturated DMF solution with 1.2 M trifluoroethanol on a glassy carbon electrode (680 mV overpotential) at a TON of 6.2, and the pendant NH moiety was suggested to stabilize the CoI–CO₂ adduct [73].

The Fe¹ catalyst containing 2,9-bis(2-hydroxyphenyl)-1,10-phenanthroline [Fe¹(dophen)]⁻ yields HCOOH at 74% FE, as well as oxalate (7%) and CO (13%) as minor byproducts, upon electrolysis in dimethyl sulfoxide (DMSO) at −1.76 V vs. SCE on a carbon electrode (Scheme 9) [74]. An iron(III) complex of 6,6′-di(3,5-di-tert-butyl-2-hydroxybenzene)-2,2′-bipyridine (Fe(III)Cl(¹⁻dhbpy)) was also reported to catalyze the reduction of CO₂ to formate in the presence of an added proton source (PhOH; FE = 68%, TON = 2.7, t = 10 h), whereas, in the absence of acid, only CO is formed (FE = 1.1%, TON = 3, t = 15 h) [75].

Recently, Lau and Robert reported Co and Fe quaterpyridine complexes (Scheme 10), [M(qpy)(OH₂)²⁺ (qpy = 2,2′:6′:2″:6″-quaterpyridine), as catalysts for CO₂-to-CO electroreduction in acetonitrile with a selectivity of >95% in the presence of phenol at low overpotentials of 140 and
240 mV, respectively, and an impressive turnover frequency (TOF) of $3.3 \times 10^4$ s$^{-1}$ was reported for the Fe catalyst [76].

Scheme 10. Structures of $\text{[Fe I(dophen)]}$ and $\text{[Mn(L)(CO)Br}_3$ and its derivatives with various pendant substituents [77–87]; $\text{L}$—$2,2'$-bipyridine or $4,4'$-dimethyl-$2,2'$-bipyridine.

Chardon-Noblat and Deronzier et al. reported $\text{fac-Mn(L)(CO)Br}$ complexes ($\text{L} = 2,2'$-bipyridine or $4,4'$-dimethyl-$2,2'$-bipyridine) as an active electrocatalyst for CO$_2$ reduction (Scheme 11) [77,78]. Controlled-potential electrolysis with Mn(L)(CO)$_3$Br ($\text{L} = 2,2'$-bipyridine) at $-1.40$ vs. SCE (420 mV overpotential) in ACN with 5% H$_2$O converts CO$_2$ into CO quantitatively, while CO is also selectively obtained (TON = 34) with $\text{R} = \text{Me}$. Kubiak et al. later reported the activity of Mn(L)(CO)$_3$Br bearing other substituents (R) on L in the presence of weak acids [79]. With $\text{R} = \text{t-buty1}$, CO is produced at quantitative FE (estimated TOF of 340 s$^{-1}$) in controlled-potential electrolysis at $-2.2$ V vs. SCE with 1.4 M trifluoroethanol. When $\text{L} = 6,6'$-dimesityl-$2,2'$-bipyridine, CO is selectively produced at high FE in electrolysis and a TOF of $5 \times 10^3$ s$^{-1}$ in acetonitrile also containing 1.4 M trifluoroethanol.

Scheme 11. Structures of $\text{Mn(L)(CO)Br}_3$ and its derivatives with various pendant substituents [77–87]; $\text{L} = 2,2'$-bipyridine or $4,4'$-dimethyl-$2,2'$-bipyridine.
When pendent proton sources are introduced in proximity to the metal center on Mn(L)(CO)$_3$Br, i.e., L = 4-phenyl-6-(1,3-dihydroxybenzen-2-yl)-2,2′-bipyridine (Scheme 11), the catalyst is active for CO$_2$ reduction in acetonitrile at $-1.8$ V vs. SCE without added acids, producing both CO (70% FE) and HCOOH (22% FE) [80,81]. A reaction pathway involving the formation of Mn hydride via intramolecular proton transfer from the phenolic moiety was suggested. Interestingly, a similar Mn(L)(CO)$_3$Br with a single pendent hydroxyphenyl substituent on the bpy ligand selectively produces CO at 76% FE at 540 mV overpotential in electrolysis in acetonitrile containing 5% H$_2$O [82]. The reactivity of the similarly structured Mn(I)-tricarbonyl catalysts bearing two and three acidic hydroxyphenyl functions was also compared in the presence of added acids (H$_2$O, 2,2,2-trifluoroethanol (TFE), and phenol), and the product (CO, HCOOH, and H$_2$) distribution was dependent on the strength of the added acid. [81,83].

Recently, a series of fac-Mn(CO)$_3$ catalysts bearing imidazolium-functionalized bipyridine, {[Mn[bpyMe(lmMe)](CO)$_3$Br]$^+$ (Scheme 11), were found to demonstrate a superior reactivity (FE = approximately 70%) toward CO$_2$ reduction in comparison to the dimesityl analogue (FE = 49.6%) at a mild potential ($-1.44$ V vs. SCE) in acetonitrile with 9.25 M H$_2$O [84]. The imidazolium moiety is suggested to favor the formation of a local hydration shell which promotes more efficient protonation of the reaction intermediates [84].

An Mn-MeCN/MWCNT catalytic cathode ([Mn-MeCN] = [Mn][4,4’-di(1H-pyrrolyl-3-propylcarbonate)-2,2′-bipyridine][CO$_3$(MeCN)]$^+$ and MWCNT = multi-walled carbon nanotube), prepared by loading the functionalized fac-Mn(CO)$_3$ catalysts (Scheme 11) onto conductive MWCNTs, promotes CO$_2$ reduction at a low overpotential of 100 mV in the presence of K$^+$ to produce CO at a steady rate for 48 h at $-0.39$ V (vs. RHE) [85]. The activities toward electrochemical CO$_2$ reduction of a similar catalyst bearing an amine-functionalized bpy ligand, fac-Mn(apbpy)(CO)$_3$Br (apbpy = 4-(4-aminophenyl)-2,2′-bipyridine), were studied under both heterogeneous and homogeneous conditions [86,87]. A glassy carbon electrode (GCE) functionalized with the complex was found to produce CO electrocatalytically in aqueous acetonitrile at a TON 30 times higher than that in homogeneous condition [86]. When grafted electrochemically onto carbon cloth, the catalyst also reduces CO$_2$ to syngas in aqueous solution (FE for CO and H$_2$ = 60% and 40%, respectively) at $-1.35$ V and a TON of up to 33,200 in 10 h [87].

Multinuclear catalysts of first-row transition metals draw much attention, as their multiple reaction centers are considered potentially more effective for mediating the simultaneous reduction of more than one CO$_2$, thus leading to the formation of C-2 (or higher) products. Kubiak reported a number of multinuclear nickel and copper phosphine complexes as electrocatalysts for CO$_2$ reduction (Scheme 12). The catalyst [Ni$_2$(μ-$\text{CNMe})$(CNMe)$_2$(dppm)$_2$] (dppm = 1,1-bis(diphenylphosphino)methane) operates at $-0.87$ V vs. SCE [88]. The similar dinuclear nickel complex [Ni$_2$(μ-$\text{CNR})$(CNR)$_2$(μ-dppa)$_2$] (dppa = bis(diphenylphosphino)amine; CNR = isocyanide ligand) also catalyzes CO$_2$ reduction [89]. However, these catalysts suffer from carbonylation upon extended cycles of catalysis [88]. Trinuclear nickel clusters [Ni$_3$(μ$_3$-$\text{I})(\mu_3$-$\text{CNR})$(μ$_2$-$\text{dppm})$_3$] were also found to catalyze CO$_2$ selective reduction to CO and CO$_3^-$ at $-1.08$ to $-1.18$ V vs. SCE [90,91]. The binuclear copper complexes [Cu$_2$(μ-$\text{PPh}_2$)py(MeCN)$_2$][PF$_6$]$_2$ (at $-1.53$ V vs. SCE) and [Cu$_2$(μ-$\text{PPh}_2$)py(py)$_2$][PF$_6$]$_2$ (PPh$_2$py = 3-diphenylphosphino-2,2′-dipyridyl) were also reported to be active electrocatalysts for CO$_2$ reduction [92]. More recently, the [FeFe]-hydrogenase model, [(μ-bdt)Fe$_2$(CO)$_6$] (bdt = benzene-1,2-dithiolato), was found to demonstrate distinctive activity for electroreduction of CO$_2$ in acetonitrile in the presence of CH$_3$OH or H$_2$O as the proton source at an estimated maximum TOF of 195 s$^{-1}$ [93]. Controlled-potential electrolysis using the catalyst under optimized conditions produces HCOOH at a good Faradaic yield of 88% as the major product (selectivity ≈ 81%), together with a small amount of CO (selectivity ≈ 11%) and H$_2$ (selectivity ≈ 8%) [93].

Despite the formation of C-2 or longer hydrocarbons being reported when electrode modified with nanocatalysts, C-2 products are less common for the electroreduction of CO$_2$ on molecular catalysts. Apart from the abovementioned Cu(TDMPP) supported on porous polytetrafluoroethylene- treated carbon fiber paper, which reduces CO$_2$ to hydrocarbons (methane and ethane) [71], so far, only a dinuclear copper(I) complex, [Cu$_2$(L)$^{2+}$ (HL = [N-(2-mercaptopropyl)N,N-bis(2-pyridyl)methyl)amine]), was reported to produce a tetranuclear copper(II) complex bearing two CO$_2$-derived oxalate groups upon
reaction with atmospheric CO$_2$ [94]. Treatment of the oxalate-bridged copper(II) complex with a soluble lithium salt in acetonitrile quantitatively produces lithium oxalate, and a subsequent electrochemical reduction of the copper(II) complex regenerates the initial dinuclear copper(I) compound, which reacts again with CO$_2$ and demonstrates six turnovers (producing 12 equivalents of oxalate) at an applied potential of $-0.03$ V vs. NHE in 7 h [94].

3. Functionalization of Carbon Dioxide

In parallel, chemical processes for using CO$_2$ as a renewable, non-toxic, and cost-efficient feedstock for producing fine chemicals are emerging [95–100]. Confined by the kinetic inertness of CO$_2$, widely applied CO$_2$ functionalization processes include the industrial preparation of urea, salicylic acid, inorganic carbonates, cyclic/acyclic organic carbonates, and pigments, as well as application as an additive in methanol synthesis [95–102]. Therefore, novel and efficient catalytic processes for CO$_2$ functionalization are highly valuable. Two major approaches for the functionalization of CO$_2$, i.e., “horizontal” and “diagonal” (reductive) approaches, evolved, and they both require the use of high-energy co-reactants, catalysts, and often stringent reaction conditions to overcome the kinetic barrier (Scheme 13) [96–105].
which usually proceed under mild conditions (room temperature and 1 atm), were much less
with Cu [132,133], Ni [133–139], and Pd [140–145] catalysts, e.g., (a) substituted carboxylic acid from
substituted arylhalide [139,140], benzyl chloride [134], alkynes [135,136], allenes [137,138], and
organosalt or ionic liquid with aziridine or epoxide [157,158].

organocatalysts, e.g., (a) organic N-heterocyclic bases (DBU) for coupling with primary amino alcohol to oxazolidines [150–152] and carboxylation of cyclopentadiene [153]; (b) N-heterocyclic carbenes (iPrNHC) for coupling with epoxide, aziridine, or propargyl alcohol to yield heterocycles and carbonates [154–156]; and (c) organosalt or ionic liquid with aziridine or epoxide [157,158].

3.1. Horizontal Functionalization of CO

A number of metal-catalyzed reactions, which utilize CO₂ as a single-carbon (C-1) feedstock,
were reported, and they require usually high pressure and temperature to proceed. In these reactions,
functionalization occurs “horizontally” via simple bond formation without changing the formal
oxidation state of the CO₂ carbon, typically giving products such as R–X–C(O)O–R′ (X = O, N, or C)
with limited variety (Schemes 13 and 18). For example, porphine [106–112] and salen-type [113–119]
complexes catalyze the coupling of CO₂ with epoxide to cyclic [113,114] and polycarbonates [115–119].
The reactions of CO₂ with amine-containing nucleophiles were studied (Scheme 14), mainly using
precious-metal (Ag [120,121], Pd [122–124], and Ru [125,126] or organotin [127,128] (Sn)) catalysts,
e.g., (a) oxazolidinones from aziridine [129], 1,2-aminooalcohols [127], and α-allyl amines [124]; (b)
benzoxazin-2-ones from α-alkynylanilines [120,121]; (c) carbamates from amine/allylic chloride [122,123],
amine/alkyne [130], and N-substituted propargylamine [126]; and (d) urea or urethane from primary
amine [128,131]. The carboxylation of carbon nucleophiles with CO₂ was studied (Scheme 15), mainly
with Cu [132,133], Ni [133–139], and Pd [140–145] catalysts, e.g., (a) substituted carboxylic acid from
arylhalide [139,140], benzyl chloride [134], alkynes [135,136], allenes [122], and alkenes [132,146];
(b) ester from alkyne/allylic chloride [133], phenylpyridine [147], and aryl methane [148]; and (c)
lactone from diene [142,149], 2-hydroxystyrene [144], allenes [138], and alkynes [137,138]. Similar
CO₂ functionalization was also performed using organocatalysts, e.g., (a) organic N-heterocyclic bases (DBU) for coupling with primary amino alcohol to oxazolidines [150–152] and carboxylation of cyclopentadiene [153]; (b) N-heterocyclic carbenes (iPrNHC) for coupling with epoxide, aziridine, or propargyl alcohol to yield heterocycles and carbonates [154–156]; and (c) organosalt or ionic liquid with aziridine or epoxide [157,158].

3.2. Electro- and Photocatalytic CO₂ Functionalization

In contrast to chemical approaches, electro- and photocatalytic functionalizations of CO₂,
which usually proceed under mild conditions (room temperature and 1 atm), were much less
investigated. In these reactions, CO₂ carbon was mostly incorporated with substrates without
changing its oxidation state. Duñach et al. reported the Ni-catalyzed electrochemical carboxylation
of alkynes and diynes, as well as electro-coupling with epoxides and aziridines under 1 atm
CO₂, using Ni-L (L = bpy, cyclam, PMDTA) catalysts and an Mg sacrificial anode (Schemes 14
and 16) [159–163]. Notably, electrocatalytic formylation of dimethyl amine (DMA) to DMF
was reported using Ru(bpy)₂(CO₂)₂ [164]. Visible-light-driven carboxylation of aryl halides [165] and
alkenes [166] was carried out using Pd(OAc)₂/PR₃/Ir(ppy)₂(dtbbpy)(PF₆) [165] and Rh(PPh₃)₃X
or [Rh(PR₃)₂Cl]₂[Ru(bpy)₃]²⁺ (R = Cy or Ar; X = OAc, Cl, or H) [166] with iPr₂EtN as the
sacrificial donor (Scheme 17). Ultraviolet (UV)-driven α-carboxylation of tertiary N-benzylpyperidines
C₅H₅N(CH₂Ph) and carboxylation of alkones were achieved using p-terphenyl/trifluoroacetate [167]
and diphenylxanthone/Cu(iPrNHC)Cl [168], respectively.
3.2. Electro- and Photocatalytic CO\textsubscript{2} Functionalization

In contrast to chemical approaches, electro- and photocatalytic functionalizations of CO\textsubscript{2}, which usually proceed under mild conditions (room temperature and 1 atm), were much less investigated. In these reactions, CO\textsubscript{2} carbon was mostly incorporated with substrates without changing its oxidation state. Duñach et al. reported the Ni-catalyzed electrochemical carboxylation of alkynes and diynes, as well as electro-coupling with epoxides and aziridines under 1 atm CO\textsubscript{2}, using Ni-L (L = bpy, cyclam, PMDTA) catalysts and an Mg sacrificial anode (Schemes 14 and 16) [159–163]. Notably, electrocatalytic formylation of dimethyl amine (DMA) to DMF was reported using Ru(bpy)\textsubscript{2}(CO)\textsubscript{2} [164]. Visible-light-driven carboxylation of aryl halides [165] and alkenes [166] was carried out using Pd(OAc)\textsubscript{2}/PR\textsubscript{3}/Ir(ppy)\textsubscript{2}(dtbpy)(PF\textsubscript{6}) [165] and Rh(PPh\textsubscript{3})\textsubscript{3}X or [Rh(PR\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}/[Ru(bpy)\textsubscript{3}]\textsuperscript{2+} (R = Cy or Ar; X = OAc, Cl, or H) [166] with iPr\textsubscript{2}EtN as the sacrificial donor (Scheme 17). Ultraviolet (UV)-driven α-carboxylation of tertiary N-benzylpiperidines C\textsubscript{5}H\textsubscript{10}N(CH\textsubscript{2}Ph) and carboxylation of alkenes were achieved using p-terphenyl/trifluoroacetate [167] and diphenylxanthone/Cu(iPrNHC)\textsubscript{Cl} [168], respectively.

![Scheme 14. Examples of metal-catalyzed CO\textsubscript{2} functionalization with amine-containing nucleophiles [120–131].](image)

![Scheme 15. Examples of metal-catalyzed carboxylation of carbon nucleophiles with CO\textsubscript{2} [132–158].](image)

![Scheme 16. Examples of electrocatalytic coupling of CO\textsubscript{2} with various carbon nucleophiles [161–163].](image)
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achieved using p-terphenyl/trifluoroacetate [167] and diphenylxanthone/Cu(iPrNHC)Cl [168], respectively.

Scheme 16. Examples of electrocatalytic coupling of CO2 with various carbon nucleophiles [161–163].

Scheme 17. Examples of photocatalytic carboxylation of carbon nucleophiles with CO2 [164–168].

3.3. Diagonal (Reductive) CO2 Functionalization

While, in the above “horizontal” transformations, the CO2 carbon is functionalized with its formal oxidation state unchanged, the “vertical” reduction of CO2 very often results in a lower oxidation state and, thus, higher-energy products, such as CO, formic acid/formate, methanol, and methane, in which no new bonds, other than C–H, are formed to the CO2 carbon (Scheme 18) [19,23–26]. For CO2 functionalization processes to be more versatile and widely applied, the spectrum of products directly obtained from CO2 has to be broadened in terms of functionalities and energy. Thus, a “diagonal” reductive approach, where CO2 is reacted in a concerted manner with a nucleophilic functionalization reagent and a reducing agent, was proposed and explored [98,169,170].

Recently, reductive coupling of CO2 with amine-type co-reactants emerged as a novel approach for accessing products bearing deoxygenated carbons, e.g., N–C(O)H, originated from CO2 (Scheme 19). Examples of metal-catalyzed N–H formylation with CO2 are shown in Table 3, and the structures of selected catalysts are shown in Scheme 20. The formylation of an N–H bond of primary or secondary amines to yield formamide derivatives was reported using precious-metal (Ir, Pd, Pt, and Ru) [164,171–176] catalysts, e.g., (PPh3)3Ir(CO)Cl [167], PdCl2 [172], [Pt2(µ-dppm)] (dppm = bis(diphenylphosphino)methane) [173,177], RuCl2(PMe3)4 [178] RuCl2(dppe) (dppe = bis(diphenylphosphino)ethane) [164,179], and Ru(PNP)(CO)(H)Cl (PNP = N,N-bis(2-diphenylphosphinoethyl)methylamine) (Scheme 20), and H2 as the reductant at a usually moderate to high turnover number (TON). Similar N–H formylation was also explored using non-precious-metal catalysts, particularly with phosphine ligands, e.g., MX2/dmpe (M = Co, Cu, Fe, Ni, and Mn; X= Cl–, CH3CO2– and acac–; dmpe = bis(dimethylphosphino)ethane) [180], Cu(PPh3)2Cl [141,150], M(BF4)2/PP3 (M = Fe and Co; PP3 = tris[2-(diphenylphosphino)ethyl]phosphine), and Fe(BF4)2/PAr3 (PAr3 = tris(2-(diphenylphosphino)phenyl)phosphine) [19,181–183]. A molybdenum sillyphosphine hydride complex, [MoH5(Si(Ph)[Ph2PCH2CH2F(Ph)C6H4-3-4-5])]2, also catalyzes DMF production from DMA and CO2 [184]. The formylations of aniline (NH2Ar) and ammonia (NH3) were demonstrated using RuCl2(PMe3)4 [185,186], [Ru(triphos)(tmm)] [187], and IrCl(CO)(PPh3)3 [188] with H2 as the
reductant. Amine–CO2 reductive coupling was also performed using hydrosilane (R3Si–H) or hydroborane (R2B–H) as the reductant on metal (Cu, Fe, Ni, and Rh) [189–193] catalysts such as [Ni(μ-H)(dippe)]2 (dippe = 1,2-bis(diisopropylphosphino)ethane) [192] and Cu(iPr-NHC)(OtBu) [193] as reductants. Recently, reductive coupling of CO2 with amines and 0-phenylenediamines was achieved using organo-base (TBD) [197,198], iPrNHC [199,200], and proazaphosphatrane (VBMe) [201] to produce formamides [196,199], formamidines [200], tertiary methylamines, and methylene diamines [198,201] using hydrosilane (PhSiH3) or hydroborane (9-BBN) as reductants (Scheme 22).

**Scheme 18.** Horizontal and diagonal (reductive) approaches for CO2 functionalization [19,23–26].

**Scheme 19.** Example of metal-catalyzed N–H bond formylation with CO2 [185–188].
Organocatalysts for reductive coupling of CO$_2$ and amines [197–201].

Scheme 20. Transition-metal catalysts for reductive coupling of CO$_2$ and amines [189–193].

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Table 3. A comparison of metal-catalyzed N–H formylation of selected primary and secondary amines with CO$_2$. dppm—bis(diphenylphosphino)methane; dppe—bis(diphenylphosphino)ethane; PNP—N,N-bis(2-(diphenylphosphino)ethyl)methyamine; dmpe—bis(dimethylphosphino)ethane; PAr$_3$—tris[2-(diphenylphosphino)ethyl]phosphine; PMHS—1,2-bis(diisopropylphosphino)ethane.

| Catalyst | Amine | P CO$_2$/H$_2$ (T) Bar (°C) | Reductant | TON/Yield (%) | Reference |
|----------|-------|-----------------------------|-----------|--------------|-----------|
| IrCl(CO)(PPPh$_3$)$_2$ | Me$_2$NH | 27/27 (125) | H$_2$ | 1200 | [188] |
| PdCl$_2$ | Me$_2$NH | 40/80 (170) | H$_2$ | 34 | [172] |
| [Pt$_2$(μ-dppe)$_3$] | Me$_2$NH | 12/94 (75) | H$_2$ | 1460 | [173,177] |
| RuCl$_2$(dppe)$_2$ | Me$_2$NH | 130/85 (100) | H$_2$ | 74,000 | [164] |
| RuCl$_2$(PMe$_3$)$_4$ | Me$_2$NH | 130/80 (100) | H$_2$ | 370,000 | [178] |
| [MoH$_3$][Si(Ph)]$_3$[Ph$_2$PCH$_2$CH$_2$P(Ph)$CH_2$N$_2$H$_2$] | Me$_2$NH | 30/20 $^a$ (110) | H$_2$ | 115 | [184] |
| Fe(BF$_4$)$_2$·6H$_2$O/PP$_3$ | Me$_2$NH | 30/60 | H$_2$ | 727 | [181] |
| Co(BF$_4$)$_2$·6H$_2$O/PP$_3$ | Me$_2$NH | 30/60 | H$_2$ | 1308 | [182] |
| Fe(BF$_4$)$_2$·6H$_2$O/PAr$_3$ | Me$_2$NH | 30/60 | H$_2$ | 5104 | [183] |
| Rh$_2$(OAc)$_2$·K$_2$CO$_3$ | PhCH$_2$NH$_2$ piperidine | 1 $^a$ (50) | PhMe$_2$SiH | 41% | [191] |
| | PhNH$_2$ | 43% | |
| | | 34% | |
| [Ni(μ-H)(dppe)$_2$]/BEt$_3$ | PhCH$_2$NH$_2$ (PhCH$_2$)$_2$NH piperidine | 1 $^a$ (80) | Et$_3$SiH | 85% | [192] |
| | | 47% | |
| | | 52% | |
| Cu(OAc)$_2$·H$_2$O/Bz[P$_2$]$_2$ | Piperidine | 1 $^a$ (80) | PMHS | 11,700/94% | [189] |
| Fe(acac)$_2$·P(C$_2$H$_4$PPH$_3$)$_2$ | (Ph)(Me)NH | 1 (RT) | PhSiH$_3$ | 95% | [190] |
| Cu(PrNHC)(O’Bu) | (Ph)(Me)NH | 1 $^a$ (35/65) | H-Bpin | 81% | [193] |
| | Ph(CH$_2$)$_2$NH$_2$ | 98% | |
| | (PhCH$_2$)$_2$NH | 90% | |

$^a$ Unit = atm; $^b$ total pressure.
Scheme 20. Transition-metal catalysts for reductive coupling of CO2 and amines [189–193].

More recently, non-carbonyl or fully deoxygenated products, e.g., formamidines (RN = C(H)NR′₂) and methylamines (R₂NCH₃) were obtained at elevated temperature and pressure (Scheme 21) from o-phenylenediamines with RuCl₂(dppe)₂ [194], as well as from primary and secondary amines with Ru(acac)₃/triphos [195] or Ru(triphos)(tmm) [187], [RuII(dmso)₄Cl₂]/P(nBu)(Ad)₂ [196], and Zn(iPrNHC)Cl [196] using H₂ and PhSiH₃ as reductants. Recently, reductive coupling of CO₂ with amines and o-phenylenediamines was achieved using organo-base (TBD) [197,198], iPrNHC [199,200], and proazaphosphatrane (VBMe) [201] to produce formamides [196,199], formamidines [200], tertiary methylamines, and methylene diamines [198,201] using hydrosilane (PhSiH₃) or hydroborane (9-BBN) as reductants (Scheme 22).

Scheme 21. Examples of non-carbonyl products formed via reductive coupling of amines with CO₂ [194–196].

Scheme 22. Organocatalysts for reductive coupling of CO₂ and amines [197–201].

4. Summary and Outlook

While CO₂ utilization remains a major scientific challenge, it is also a promising means for providing petroleum substitutes, thus achieving sustainable and carbon-neutral resource utilization, in face of the current rising atmospheric CO₂ level. The direct reduction and the concerted reductive functionalization of CO₂ enable us to assess a broad spectrum of products which are higher in energy and varied in functionality, in comparison with the “horizontal” pathways. However, the search of novel, economic, and environmentally friendly catalysts, which circumvent the current reaction bottlenecks, will be highly important in terms of the access to desirable products, as well as the enhancement of catalyst stability and energy efficiency. Much is to be done for molecular catalysts with respect to understanding how the coordination spheres will facilitate yielding the desired products of varied oxidation states on the CO₂-derived carbon, particularly in obtaining C-2 or higher hydrocarbons [30,53–55,67,68,71,80–87,94,98,169–193]. For the reductive transformations of CO₂ to be sustainably driven by renewable energy sources, the exploration of direct photo-driven redox catalysis using systems of photosensitizer–catalyst combinations without precious metals [17–20] and the development of catalytic electrodes bearing the immobilized macromolecular or molecular catalysts [24,62–65,69–71,85–87] will be essential, such that the technology will be further advanced and materialized in the form of photoelectrochemical cells [31].

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