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Review Article

Organic functionalization of metal catalysts: Enhanced activity towards electroreduction of carbon dioxide

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Abstract
Electrochemical reduction of carbon dioxide has been attracting extensive interest due to its fundamental significance both in environmental protection and in energy storage. In this review, recent progress in the manipulation of the catalytic activity and selectivity of various transition metals towards CO_2 reduction reaction (CO_2RR) is summarized within the context of deliberate surface functionalization by select organic ligands. This is primarily manifested in three effects, interfacial charge transfer, suppression of hydrogen evolution, and stabilization of key reaction intermediates. The review is concluded with a perspective of the challenges and promises in the structural engineering of metal catalysts for enhanced CO_2RR performance.

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The concentration of carbon dioxide (CO_2) in the earth's atmosphere has been increasing drastically since the era of industrial revolution, due to massive consumption of fossil fuels, which contributes significantly to global warming and abnormal global climate [1,2]. Electrochemical reduction of CO_2 to fuels is believed to be a promising route to the mitigation of such climate hazards [3–7], thanks to its high efficiency, controllable selectivity, simple electrochemical reactors and enormous potential for practical industrial applications. Importantly, the conversion of CO_2 to fuels also allows for sustainable energy conversion and storage. Yet, CO_2RR involves rather complicated reaction mechanisms, and includes a wide range of final products, such as CO, methane, ethylene, formic acid, and alcohols [8–12]. Also, because of high chemical stability of CO_2 molecules, CO_2RR is kinetically sluggish. Therefore, to facilitate the reaction, it is necessary to develop high-performance, robust catalysts. This necessitates a good understanding the reaction mechanism of CO_2RR. Extensive research has shown that CO_2RR involves at least three key sequential steps: (i) adsorption of CO_2; (ii) surface diffusion of CO_2, and electron and proton transfer to CO_2; and (iii) desorption of products [13–17]. Of these, step (ii) is generally believed to be the rate-determining step (RDS) [18,19]. Tafel slope is an important experimental parameter in the study of CO_2RR mechanism. For instance, a Tafel slope of ca. 120 mV/dec typically suggests that RDS involves the first one-electron reduction of adsorbed CO_2 to form the CO_2^{*-} intermediate, whereas a Tafel slope of ca. 60 mV/dec suggests that RDS is likely the protonation of CO_2^{*-} [20–23].

Transition metals have played a critical role in CO_2RR. Prior research has shown that the electrocatalytic activity of metal (nanoparticle) catalysts depends on the catalyst structure, morphology, and elemental composition, as highlighted in a series of recent reviews [24–26]. Remarkably, recent research has also shown that deliberate surface engineering of the metal catalysts with select organic capping ligands can also be exploited as a new, effective strategy in manipulating the CO_2RR activity [27•-30••], as motivated by breakthroughs in a range of important reactions in electrochemical energy conversion and storage, such as formic acid oxidation and oxygen reduction reactions [31–38]. In this minireview, we will summarize the latest, key research progress of CO_2RR based on surface functionalization of several leading metal catalysts (i.e., Au, Ag, Pd, and Cu) with organic capping ligands, and conclude with a perspective of the significance of surface engineering of nanoparticle catalysts for enhanced CO_2RR performance.

Gold has been found to exhibit apparent activity towards CO$_2$RR. In one study, Mikoshiba et al. [28•] modified a Au electrode with a self-assembled monolayer (SAM) of thiol-terminated imidazolium ion through Au-S interfacial bonds (Figure 1a). CO$_2$RR on the bare Au electrode yielded only CO, while the SAM-modified one produced ethylene glycol instead with a maximum faradaic efficiency (FE) of 87%. The authors also observed an exponential decay of the CO$_2$RR current density with the chainlength of the thiol ligands, signifying that the reduction current density of the SAM-modified electrode was dominated by electron tunneling through the surface capping ligands. Mechanistically, this involved the formation of an imidazolium-carboxylate intermediate, which not only reduced the energy barrier of CO$_2$RR but also suppressed hydrogen evolution reaction (HER), a significant interference in CO$_2$RR. In another study, Fang et al. [30••] investigated and compared the CO$_2$RR activity of a Au electrode before and after functionalization with three thiol derivatives: 2-mercaptopropionic acid (MPA), 4-pyridinylethanemercaptan (PEM), and cysteamine (CYS). It was found that the

PEM-Au electrode showed a two-fold increase in FE and three-fold increase in formate production, relative to bare Au. By sharp contrast, the MPA-Au electrode exhibited minimal CO$_2$RR activity with almost 100% FE for hydrogen evolution, while the CYS-Au electrode increased both CO and H$_2$ production by two folds. By analyzing the correlation between the difference of the onset potentials of HER and CO$_2$RR and the surface concentration ratio of H$^+$ to CO$_2$ using the Butler–Volmer relationship, it was found that the product selectivity of CO$_2$RR was strongly dependent on the local pH at the electrode surface, which was related with the dissociation of hydrated cations and the pK$_a$ of the MPA, PEM and CYS ligands. The enhanced current density and selectivity of formate production catalyzed by the PEM-Au electrode was ascribed to the separated proton and electron transfer reactions enabled by the PEM ligands, analogous to the catalytic actions of enzymes [39]. Specifically, on the PEM-Au electrode surface, a proton from the aqueous solution was first reduced forming an H-atom adsorbed on Au, and the electrophilic attack of CO$_2$ to the adsorbed H yielded HCO_2^*. Next, the tethered

Figure 1
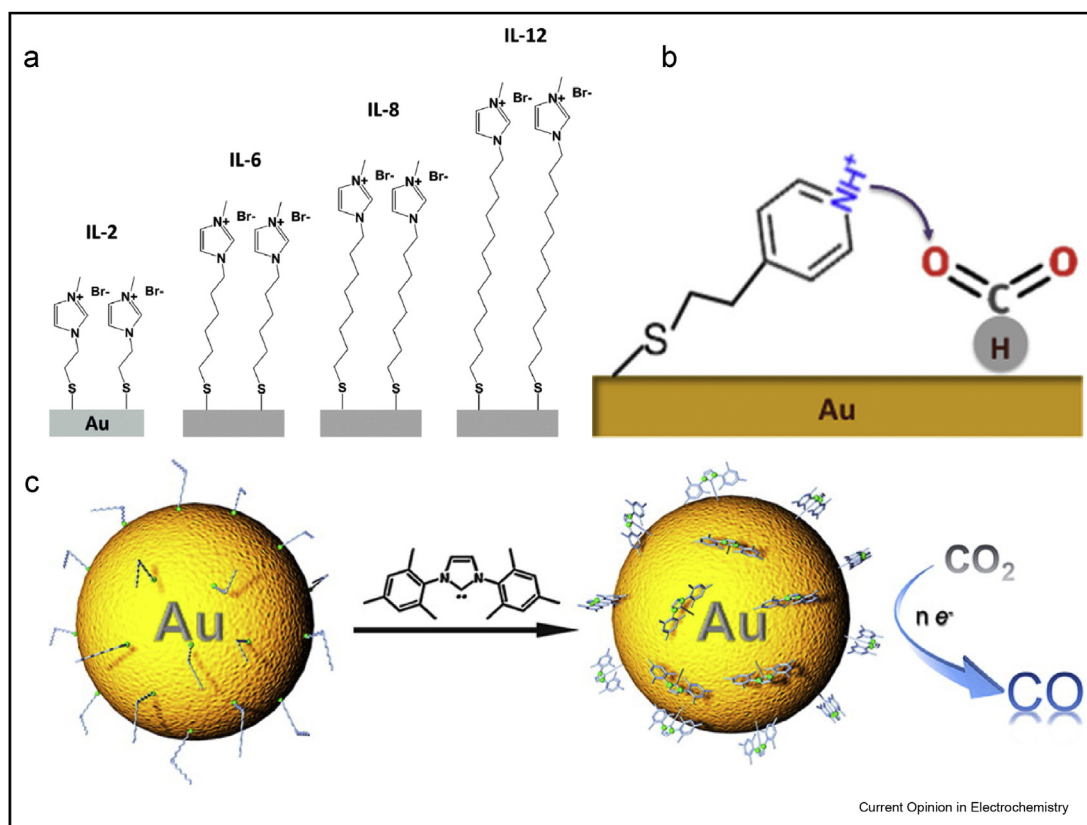
(a) Schematic of Au electrodes modified with 1-methylimidazolium-terminated SAMs (IL-2, IL-6, IL-8, and IL-12). Reproduced with permission from Ref. [28•] © 2015, Royal Society of Chemistry. (b) Proposed reaction mechanism on the PEM-modified Au surface. Reproduced with permission from Ref. [30••] © 2017, American Chemical Society. (c) Schematic of carbene ligand exchange reaction on Au nanoparticle surface. Reproduced with permission from Ref. [40••] © 2016, American Chemical Society.

pyridinium (pyrH$^+$) in the thiolate group transferred a proton to the nearby oxygen of the HCO_2^* coupled with one-electron transfer from the electrode surface. Based on such an analysis, the proton donating ability (i.e., pK$_a$) of the capping ligands was proposed to be correlated with the formate and H$_2$ production for CO$_2$RR on SAM-functionalized Au electrodes, as shown in Figure 1b.

In another study by Chang and coworkers [40••], it was found that surface functionalization of Au nanoparticles with a N-heterocyclic carbene (NHC) (Figure 1c) increased FE of CO$_2$RR to CO from 53% to 83% and current density by 7.6-fold at the overpotential of 0.46 V,

accompanied with a decrease of the Tafel slope from 138 mV/dec to 72 mV/dec. The former suggests that the RDS was 1e$^-$ reduction of adsorbed CO$_2$ to CO_2^{*-}, whereas in the latter, RDS was due to protonation of CO_2^{*-}. It is argued that the strong σ-donation from NHC to Au nanoparticles made the gold surface electron-rich, which facilitated electron transfer from Au to CO$_2$, rendering the overall reaction limited by the subsequent protonation step. In addition, the strong carbene-gold bonding interaction destabilized the gold-gold bond between neighboring Au atoms, resulting in reconstruction of the Au nanoparticle surface, an increasing number of gold defect sites, and hence enhanced kinetics for CO$_2$RR.

Figure 2
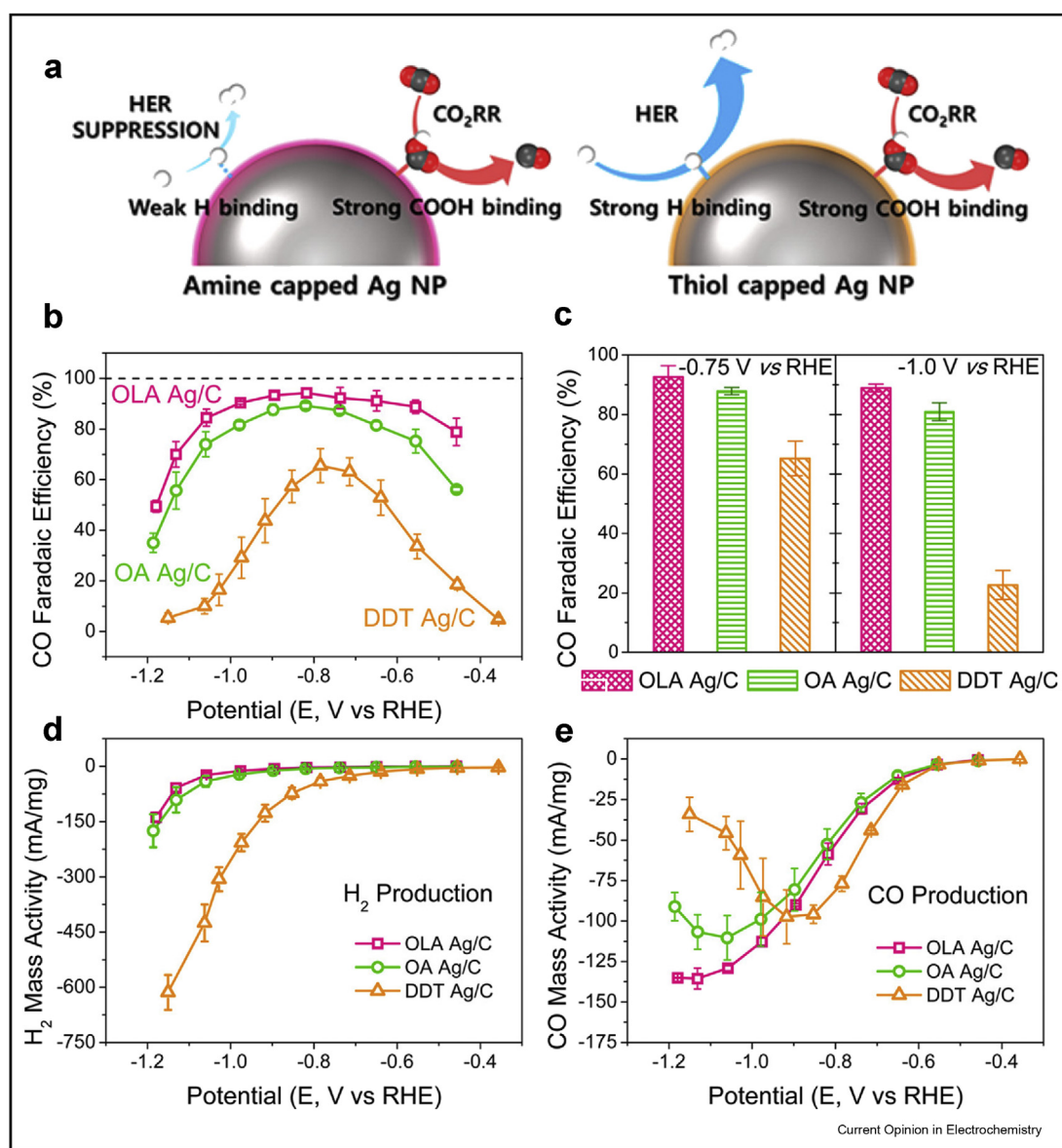
(a) Schematic of CO$_2$RR on amine- and thiol-capped Ag nanoparticles. Variation of CO FE of OLA, OA and DDT Ag/C with (b) the applied voltage and (c) fixed potential. Mass activity for (d) H$_2$ and (e) CO production of OLA, OA and DDT Ag/C at varied applied potentials. Reproduced with permission from Ref. [41•] © 2017, American Chemical Society.

Ag is also active towards CO₂RR. For instance, Hwang and co-workers [41•] developed an effective strategy to tune the electrocatalytic activity and selectivity of Ag towards CO₂RR by modulating the binding energies of the intermediates on the catalyst surfaces with the assistance of capping agents, such as oleylamine (OLA), oleic acid (OA), and dodecanethiol (DDT), as shown in Figure 2. They found that amine-functionalized Ag nanoparticles delivered a high FE of 94.2% for CO production by selectively suppressing HER, while thiol-functionalized Ag nanoparticles actually increased the HER activity. Density functional theory (DFT)

Figure 3
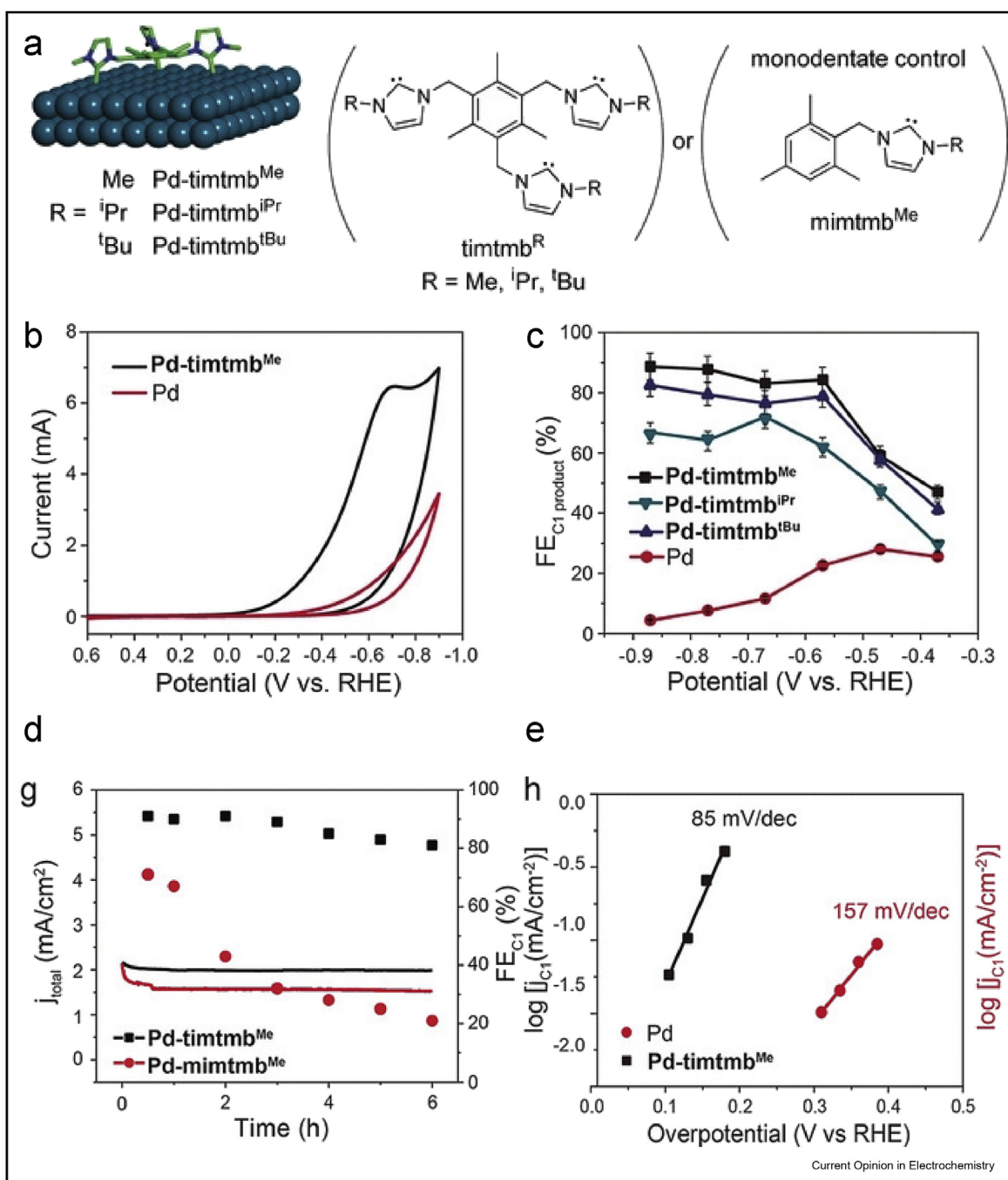
(a) Synthetic scheme for the preparation of tripodal N-heterocyclic carbenes and functionalization of palladium surfaces. (b) CV scans of Pd and Pd−timtmb^Me electrodes in CO₂ -saturated 0.5 M KHCO₃. (c) Specific current densities of C1 product by Pd and Pd−timtmb^Me electrodes. (d) Controlled potential electrolysis of Pd−mimtmb^Me and Pd−timtmb^Me electrodes at −0.57 V over a 6 h time course. (e) Tafel plots of Pd and Pd-timtmb^Me electrodes. Reproduced with permission from Ref. [42] © 2018, Wiley.

calculations showed that the amine-capping ligands stabilized the COOH intermediate, destabilized hydrogen binding and effectively suppressed HER, while thiol-functional ligands indiscriminately increased both HER and CO_2RR, which lowered the FE for CO production.

Pd represents another unique catalyst for CO_2RR. For instance, the Chang group [42] observed enhanced CO_2RR activity and selectivity of a Pd foil electrode by functionalization with tridentate NHC derivatives (Pd—timtmb^{Me}, Pd—timtmb^{iPr} and Pd—timtmb^{tBu}, where timtmb was 1,3,5-tris(1-alkylimidazoliummethyl)-2,4,6-trimethylbenzene, and Me, iPr and tBu were the substituent groups on the NHC ligand) (Figure 3a). Experimentally, it was found that the Pd—timtmb^{Me} electrode exhibited a 32-fold increase in the activity of CO_2RR to C1 products with an FE of 86%, as compared to that without surface functionalization (FE = 23%) (Figure 3b and c). In fact, all three substituent groups of Me, iPr and tBu modulated the selective production of C1 products of CO_2RR. In addition, the Pd electrode functionalized with tridentate NHC ligands exhibited much enhanced stability, as compared to that with monodentate NHC (Pd—mimtmb^{Me}, where mimtmb was 2-(1-alkylimidazoliummethyl)-1,3,5-trimethylbenzene) (Figure 3a,d). Theoretical calculations showed that the energy barrier of the formation of COOH* was 0.85 eV for Pd-timtmb^{Me}, much lower than that for the naked Pd surface (1.23 eV), suggesting more energetically favored formation of COOH* on Pd-timtmb^{Me}. In addition, the Pd foil electrode exhibited a Tafel slope of 157 mV/dec, signifying that the RDS was the formation of CO_2^{*-}, whereas the Tafel slope for Pd-timtmb^{Me} was only 85 mV/dec, suggesting that the CO_2RR kinetics was largely dictated by the protonation of CO_2^{*-} (Figure 3e). Again, this was accounted for by the strong σ-donation from the NHC ligands to Pd that effectively tuned the formation of reaction intermediates and product selectivity of CO_2RR.

Cu also plays an important role in CO_2RR. Research has shown that functionalization of Cu surface with select ligands can stabilize adsorbed intermediates (e.g., CHO, COH, etc) over CO, leading to improved selectivity of hydrocarbon production [43]. For instance, Wang and coworkers [29••] developed a general approach based on amino acid modified-Cu electrodes for the selective electroreduction of CO_2 to hydrocarbons. To demonstrate the validity of this modification approach and to rule out possible effects of Cu morphology, the authors examined three different types of Cu electrodes, i.e., a Cu nanowire film, a polished Cu foil, and an annealed Cu electrode. For all three electrodes, amino acid modification was found to suppress HER and improved the efficiency of the total generation of hydrocarbons. Theoretical calculations showed that the formation of hydrogen bond between CHO* and $-NH_3^+$ of zwitterionic glycine led to stabilization of the CHO* intermediate and enhanced the selectivity for CO_2 reduction.

In summary, recent research, highlighted by the studies cited above, has shown that surface functionalization of metal (nanoparticle) catalysts with select organic ligands can be exploited as a new, effective strategy in the manipulation of CO_2RR activity and selectivity, in addition to the conventional variables of size, shape and elemental composition. This is generally ascribed to three major effects, manipulation of the electron density of the catalyst surface by interfacial charge transfer, suppression of H_2 generation, and stabilization of key reaction intermediates (e.g., CHO* on Cu, COOH* on Ag and Pd, and HCOO* on Au).

It should be noted that prior research is mostly confined to these four metal catalysts. Thus, to further enhance the electrocatalytic performance, more in-depth investigations are desired by extending the studies to other metals and their alloys. In addition, it is critical to develop advanced *in situ/operando* characterization techniques, such as in *situ* FTIR and X-ray absorption spectroscopy, to unravel the mechanistic insights of the impact of surface functionalization of metal catalysts on the CO_2RR activity and selectivity, which, in conjunction with results from theoretical calculations, will advance our understanding of the reaction pathways. This will allow for the development of a fundamental framework for the design and engineering of high-performance catalysts for CO_2RR. The breakthroughs may be further aided by the availability of a diverse range of metal-organic bonds, such as metal-carbon (M—C, M = C and M≡C), metal-nitrogen (M—N, M = N), metal-sulfur (M—S) and metal-silicon (M—Si) bonds, that have been readily formed in organometallic complexes and metal nanoparticles [32]. Further research along this line is desired.

Conflict of interest statement
The authors declare no conflict of interest.

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