Tuning reactivity through molecular modifications of organometallic complexes on an electrode surface

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ABSTRACT: The versatility of using electrodes to control catalytic reactions heralds a new paradigm in designing chemical transformations based on molecular compounds. Functionalization of molecular compounds on an electrically addressable surface offers an additional degree of freedom in controlling a catalyst's reactivity and selectivity. Herein, we discuss the possibilities to harness electrode-supported molecular catalysts in electrocatalytic reactions and electrostatic effects observed in the surface-anchored systems recently reported. Furthermore, we summarize reported functionalization methods and outline how the proximate electrode asserts its influence on catalysis by a variety of avenues.

1. INTRODUCTION

Over the past decade, electrocatalysis has been recognized as an accessible, scalable, and sustainable tool to address commonly encountered challenges in energy conversion and chemical synthesis.[1, 2, 3] The rational design of functionalized electrodes bearing a tunable molecular moiety has become increasingly popular in electrocatalysis, hybridizing the fields of heterogeneous electrochemistry and molecular catalysis. In pursuit of potent, selective, and efficient catalysts, organometallic complexes mimicking highly efficient metalloenzymes have been brought under the spotlight for applications in electrochemical transformations.[4]

The immobilization of molecular catalysts on an electrode surface may be a solution to bridge the gap between freely dispersed molecular compounds and heterogeneous catalysts in electrochemical systems (**Figure 1**). A molecular catalyst in electrochemistry has been previously defined as either a homogenously dispersed compound in solution or active layers of molecules localized near the electrode surface.[5] The significant distinction between heterogeneous *vs.* molecular electrocatalysis is that, in the latter case, active sites are well-defined molecules.[6] Given their versatility, relatively easy tunability, and the possibility to understand their working mechanisms, homogenous organometallic complexes were introduced to electrochemical systems to increase accessibility and control reactivity.[7, 8] However, solvent incompatibility, slow diffusion rates, low electron transfer rates, and catalyst degradation remain hurdles on the road towards the optimization of catalytic activity.[9] On the other hand, heterogenous catalysts, where electrodes directly participate in electron transfer reactions, are promising for practical applications due to their robust and recyclable nature. It has been shown that immobilizing molecular catalysts onto an electrically addressable surface may help with solvent incompatibility, in addition to promoting electron transfer, simplifying the separation process of products from the catalyst, and preventing the formation of aggregates.[7, 9] Thus, an immobilized molecular catalyst is expected to be more efficient and recyclable in electrochemical synthesis than its non-immobilized counterpart. The chemically modified electrodes prepared from molecular compounds immobilized onto electrically addressable surface/electrode provide an excellent platform for obtaining potent catalysts for key transformations related to energy generation.[10-17]

This review aims to stimulate ideas and critical thinking on the rational design of chemically modified electrodes. By illustrating the unique chemical reactivity and comparing the catalytic behavior of different hybrid systems when molecular catalysts are attached to an electrode, we strive to provide a systematic view of the field. First, we will offer a technical perspective on the possible approaches to immobilize a molecular catalyst on an electrically addressable surface, mainly focusing on carbon-based electrode materials and including a few examples of metal oxide and metal surfaces. Modifications of the molecular moiety to accommodate the functionalized surface via different linkages will be elaborated next. To provide a clear starting point for those who are new to the field, we also include techniques commonly employed in characterizing the modified surfaces. We then discuss molecular electrocatalysis enabled by anchored catalysts prepared from covalent or non-covalent immobilization of the electrode surfaces. In addition to detailed methods of functionalization, a particular attention is devoted to the electrochemical control and tunability of the functionalized catalysts and their subsequent catalytic performance, especially on reactions related to energy conversion and small molecule activation. Moreover, some compelling examples discussing the effect of external electric fields in a hybrid system on catalytic turnover will be included to showcase the diversity of future applications. As this review will elaborate on the difference and connections between electrocatalysis and catalysis powered by electrostatic interactions, as well as the crucial roles of the molecular attachment involved in both cases, we aim to inspire researchers to interface organometallic chemistry, surface chemistry, and electrochemistry.

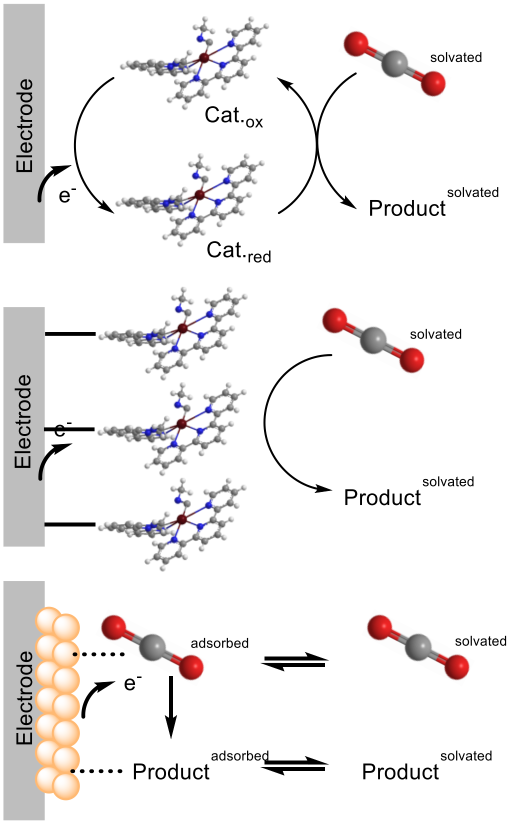

FIGURE 1. Illustration of catalytic CO_2 reduction by a homogenous (top), an immobilized (middle), or a heterogeneous (bottom) catalyst.[18] Reproduced with permission from Ref. 18. Copyright 2020 American Chemical Society.

2. OPPORTUNITIES FOR SURFACE IMMOBILIZATION

2.1 Possible sites for molecular modification on electrode surfaces

2.1.1 Carbon-based electrode surfaces

Various immobilization methods on carbon-based electrodes (e.g., graphene and carbon nanotubes) have been reported and categorized into non-covalent or covalent methods and periodic doping modification methods.[9] The coupling of organometallic complexes with carbon-based electrodes combines the stability and conductivity of carbon electrodes with the high activity and selectivity of metal complexes.[7, 19, 20] **Figure 2** depicts common strategies for functionalizing electrode surfaces represented by carbon-based electrodes. Polymer coating, adsorption, and non-covalent and covalent methods have been widely applied.[7, 21-25] To implement certain specific functionalities onto the surface via the covalent immobilization method, the surface often needs pretreatment. We will focus on the non-covalent and covalent methods for surface functionalization as they are feasible and allow for various linkages and structural diversity of molecular catalysts. The periodic doping method will not be included in this review as it is not suitable for anchoring functionalities. Non-covalent methods involve nonbonding interactions such as van der Waals forces, electrostatic interactions, hydrogen bonding, and π-π stacking interactions. Among these methods, π-π stacking between a ligand and an electrode represents a straightforward strategy of immobilizing aromatic compounds onto the electrode surface (**Figure 2**).[9, 26-29] Applications of immobilized molecular electrocatalysts via non-covalent methods in reactions related to energy conversion such as CO_2 reduction and oxygen evolution reaction (OER) have been well-studied and summarized.[9, 28-34] Despite the convenience of the non-covalent immobilization method, challenges remain in reducing catalyst leaching and aggregation to optimize the performance and durability of the electrocatalytic system.

Covalent immobilization tends to be more complicated than the non-covalent counterpart but usually provides a robust connection through covalent bonds between the surface and the molecular catalyst. Both chemical and electrochemical reactions, e.g., alkyne-azide cycloaddition, could be utilized to create covalent bonds between an electrode and an organic moiety that either serves as a ligand or originates from a pre-established organometallic complex (**Figure 2**).[9] It is also possible to functionalize the surface through other bonds such as forming ester or amide bonds with a carboxylic acid. Pretreating the electrode surface to increase the number of functional groups provides possible binding sites for metal complexes through surface conjugation.

2.1.2 Metal and metal oxide-based electrode surfaces

Metal electrodes such as Cu, Au, Ag play an essential role in electrochemical studies.[38] The intrinsic electronic structure of the metal electrode determines the electrocatalytic activity of the system, while the desorption energy of active species on the surface can be modulated by polarizing the electrode surface based on calculations.[39] In light of that, immobilization on the metal electrode surface was employed to modulate the catalytic activity. For example, Deng and coworkers triggered an electropolymerization of molecules to generate organic frameworks on the surface of a gold electrode, which created a compact interface enriched by amino groups.[40] This non-covalent modification of the metal electrode surface resulted in higher CO production and selectivity than bare gold electrode under the same conditions. To increase the available anchoring sites on metal surfaces, pre-modifications of metal are commonly required accommodated modified molecular functionality. For example, a gold surface modified by alkanethiol groups with terminal azides was functionalized by a biomimetic molecular catalyst equipped with terminal alkynes via “click reaction”.[41]

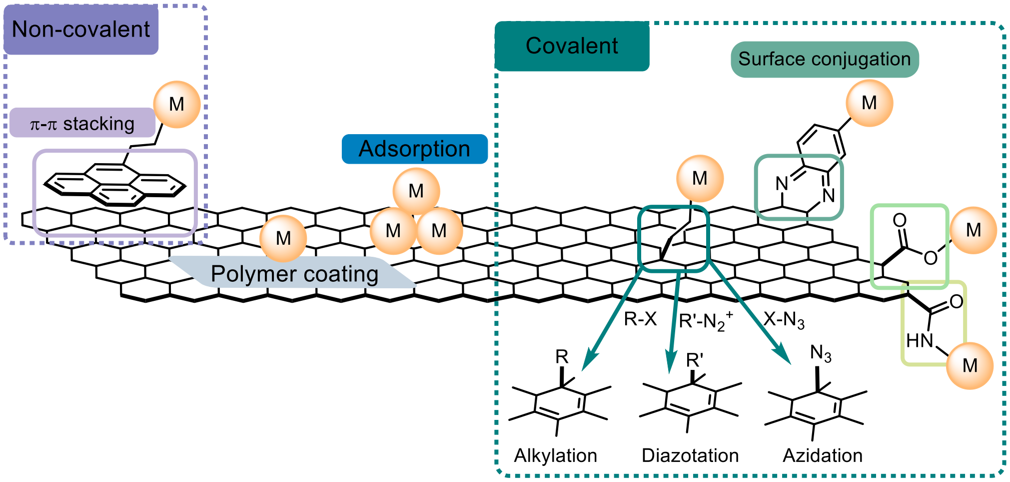

FIGURE 2. Common strategies for molecular surface functionalization are represented by the carbon-based electrode. Pretreating the surface may be necessary to provide available sites for functionalization (ex., oxidize glassy carbon electrode to increase carboxylic functionalities for the potential formation of ester or amide linkage).[7, 21-25, 35-37] Reproduced with permission from Ref. 21. Copyright 2019 American Chemical Society.

Recently, *N*-heterocyclic carbenes (NHCs) were also found to bound firmly with metal electrodes,[42-45] and displayed the potential to form length-adjustable polymer brushes binding with active species (**Figure 3a**).[45] In the recent decade, manifold immobilization strategies were developed for metal surfaces in addition to gold. Chang and coworkers directly anchored supramolecular cages of cobalt porphyrins on a copper electrode surface by using the strong interaction between thiol groups and copper (**Figure 3b**).[46] However, it is worth noting that metal surfaces tend to participate in redox reactions which cannot be fully disentangled from the activity of the immobilized complexes. In light of the growing economic concerns, precious metal surfaces are deprioritized for surface functionalization in our perspective.

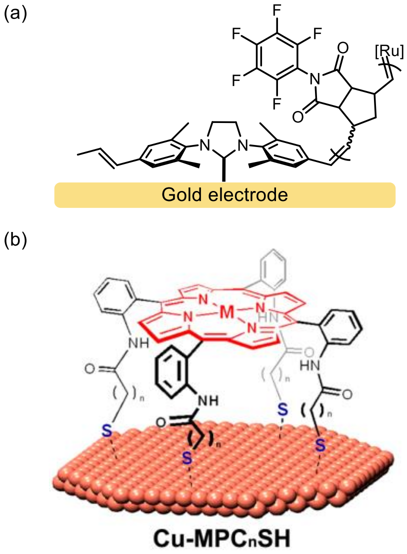

FIGURE 3. (a) N-Heterocyclic carbene modified metal surface enabling polymer brushes binding with active species. Reproduced with permission from Ref. 45. Copyright 2013 American Chemical Society; (b) Cobalt porphyrin functionalized copper electrode surface through Cu-S bonds. Reproduced with permission from Ref. 46. Copyright 2017 American Chemical Society.

Metal oxides are a promising platform for immobilization because of their accessibility, thermodynamic stability, and potential to be prepared in various nanometer-sized structures.[47] In addition to the abundant anchoring units on the surface, such as hydroxyl groups, metal oxides display highly tunable optical and electrical characteristics (e.g., transparent and electrically conductive indium tin oxide, fluorine-doped tin oxide, and semiconductive titanium oxide).[48-56] Like carbon-based electrodes, metal oxides can be used for covalent[48-52, 56] or non-covalent[53-55] immobilization. For example, anchoring sites on metal oxides surface, including oxyacids (e.g., carboxylic acids, phosphonic acids, and hydroxamic acid) and silatranes, covalently bind to metal oxide surfaces in various ways (**Figure 4**). Except for hydroxamic acids, which exhibit mono-chelating binding mode, the most popular binding mode for the abovementioned oxyacids and silatranes is bridging bidentate. These tendencies of binding mode could be analyzed by the existence or disappearance of infrared active bonds after being bound to the metal oxide surface (e.g., C=O stretching in carboxylic acids disappeared after the anchoring group followed bridging bidentate binding modes on the metal oxide surface).[57]

2.2 Modifications of molecular catalysts to enable surface attachment

The general strategy of developing a molecularly modified electrode system involves the selection of a potent catalyst that is highly active in the homogenous state, followed by configuring methods to anchor it onto the electrode surface. Depending on the electrode surface and compound picked for the reaction of interest, modifications may be needed. In the previous section, we discussed common strategies employed for electrode surfaces functionalization taking carbon-based electrode as an example (**Figure 2**).

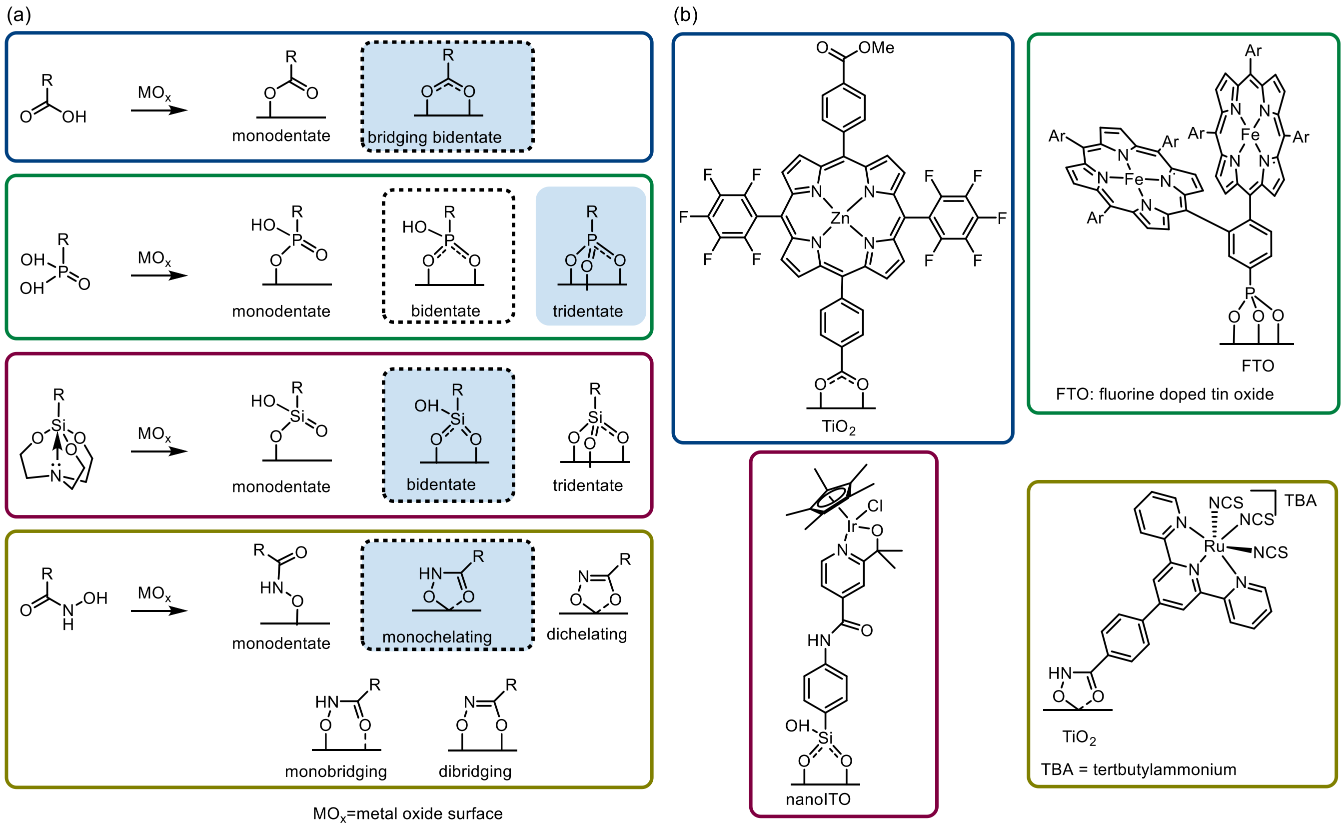

FIGURE 4. (a) Possible binding modes of a carboxylic acid, phosphonic acid, silatrane, and hydroxamic acid surface anchors to metal oxide surface (MO_x). The most favored binding modes are boxed in-dash. (b) Examples of organometallic compound immobilization for binding modes highlighted in blue.[58-62] Reproduced with permission from Ref. 58. Copyright 2017 The Royal Society of Chemistry.

To provide a detailed illustration of those strategies, a few samples demonstrating the molecular modifications to create the necessary interactions with the surface are presented in **Figure 5**. Modifications of the molecular compounds include the introduction of aromatic functionality to enhance π-π interactions (**Figure 5a**), the inclusion of amines for condensation coupling on the modified surface (**Figure 5b**), as well as forming an amide linkage (**Figure 5c**), and the presence of terminal alkyne allowing click reaction with surface azide (**Figure 5d**). Each bonding provides a specific degree of rigidity and versatility. However, some immobilization methods may not be suitable for a particular type of metal complex as the conditions required to carry out functionalization might be too harsh for the metal complex to survive. In this regard, selecting a relatively stable metal complex with compelling catalytic activity with a practical immobilization method could save a lot of effort. However, the implications on the catalytic behavior caused by the modifications made on the metal complex either to create the possible site of linkage or during the immobilization are inevitable. It is always necessary to characterize the functionalized material appropriately and compare its activity to that of the homogenous analogue.

In general, ligand structure modifications can change dramatically the catalytic behavior of an organometallic complex. Modifying the electrically addressable surface with the proper choice of a metal-ligand combination to contain functional groups that induce electronic, steric, and/or electrostatic effects will allow control over the activity of the resulting catalyst. The type of support/electrode and the type of linkage between the electrode and the ligand is also essential in providing access to electrons and the electric field.[6, 7, 9, 67] Detailed discussions on different linkages affecting the electron transfer rate, reaction pathway, and catalytic performance in small molecule activation reactions will be elaborated in **Section 3**. The hybrid system, engendered from a logical combination of a molecular catalyst and solid support via an appropriate linkage, presents a new paradigm toward catalytic material design. Therefore, aspects to consider for a rational design of an electrocatalytic system enabled by a molecularly modified electrode include (**Figure 6**) possible sites for modification on the ligand, the electrode material, the molecular linkage created for immobilization (covalent and non-covalent), and the solvent/electrolyte used. A careful examination of those components could lead to a logic approach for the hybrid catalytic material design and optimization.

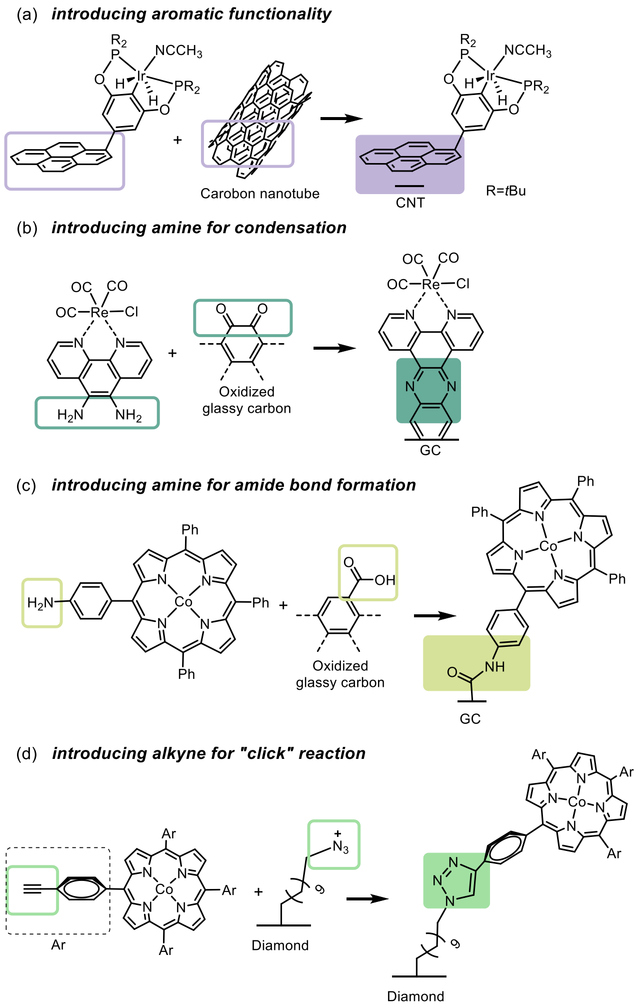

FIGURE 5. Examples of immobilizing molecular catalysts on electrode surface through molecular modifications.

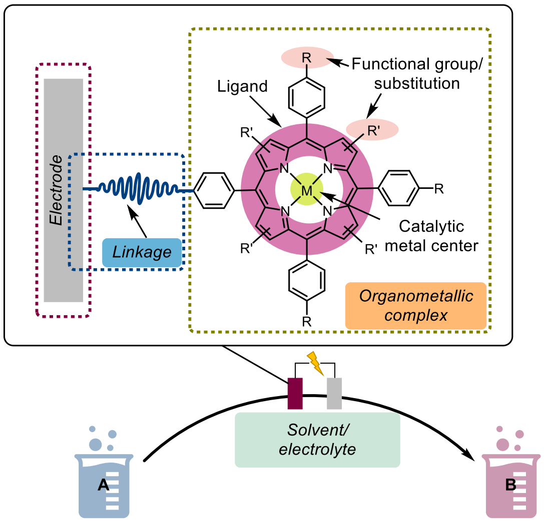

FIGURE 6. A molecularly modified electrode enabled by anchoring a catalytically active organometallic complex through a linkage. Solvent, electrolyte, and other additives or components need to be considered.[9] Reproduced with permission from Ref. 9. Copyright 2020 The Royal Society of Chemistry.

2.3 Characterization methods to study the heterogenized systems

Characterizing the interface involving covalently or non-covalently anchored molecular catalysts provides a comprehensive understanding of the hybrid system. Most organometallic complexes with redox-active metal centers or redox non-innocent functionalities can deliver electrochemical responses in cyclic voltammetry to display unique features. Besides electrochemical characterization, heavy elements and representative binding modes with the electrode surface can also be analyzed by spectroscopic techniques, such as UV-vis, IR spectroscopy, X-ray photoelectron spectroscopy, and can compensate for the lack of information in cyclic voltammetry experiments under some circumstances.

2.3.1 Cyclic voltammetry

The experiment of collecting the reversible behavior between the flowing current and linearly changed potentials with time is generally known as cyclic voltammetry (CV). Cyclic voltammetry is commonly carried out in a three-electrode system (**Figure 7a**).[68] In such a system, the working electrode will host the redox reaction of interest, and the counter electrode can balance the current flowing from the Faradaic reaction on the working electrode surface. The reference electrode will allow for accurate measurements of the working electrode potential. In the three-electrode system, researchers often utilize the Gouy–Chapman–Stern model at the interface between the working electrode and electrolyte to describe the interfacial effect (**Figure 7b**).[69] The double layer on an electrode surface includes a compact double layer within the outer Helmholtz plane (OHP) and a diffusion layer connected to ion redistribution.[70] To ensure a negligible contribution from the migration to the mass transport of the charged active species during a Faradaic reaction, an excess of supporting electrolyte is usually used to simplify the mathematical treatment of the Faradaic current and establish a uniform ionic strength throughout the solution even under steady-state Faradaic conditions.[71]

Cyclic voltammetry is a powerful tool to characterize surface-anchored molecular catalysts.[17, 48, 49, 51, 72] Unlike their solubilized counterparts that are free to move around in an electrolyte solution, anchored compounds have limited diffusion range depending on the linkage length and solvent, and usually do not diffuse through the electrical double layer. They gain or lose electrons through electron transfer due to the directional potential difference with the electrode. Therefore, the peak current of surface anchored compounds in typical cyclic voltammograms would be linearly proportional to the scan rate rather than the square root of the scan rate as for their free soluble analogues,[73] a feature that could be employed to validate that the catalysts are anchored (**Figure 8a**).[49] Furthermore, the symmetry of the i-E trace (i.e., the relationship between current and voltage during scanning) can reflect the system's chemical stability (i.e., surface anchored catalysts do not decompose or get dissolved) and electrochemical reversibility (i.e., Nernstian wave).

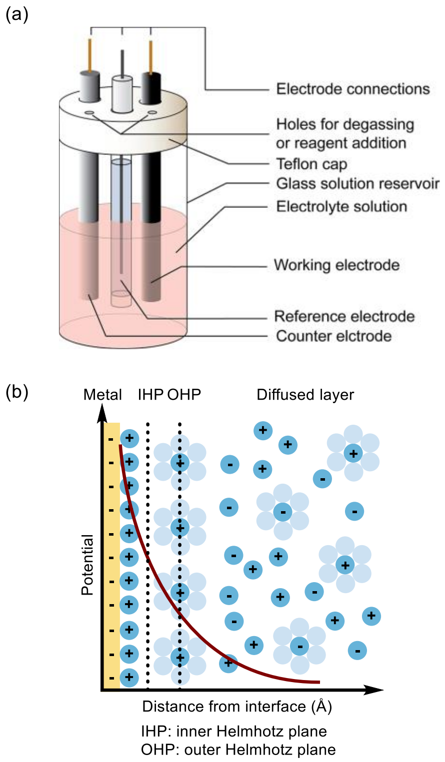

FIGURE 7. (a) Illustration of a three-electrode system for the cyclic voltammetry (CV) measurement. Reproduced with permission from Ref. 67. Copyright 2018 American Chemical Society. (b) Gouy–Chapman–Stern model at the metal-electrolyte interface. Reproduced with permission from Ref. 69. Copyright 2021 the Royal Society of Chemistry

Two parameters may be extracted from the analysis. One is the ratio between the cathodic and anodic peak current (i.e., i_{pa}/i_{pc}). Another is the separation of the two peak potentials (i.e., E_{pa} - E_{pc}). For a chemically stable system, the ratio of peak currents is generally equal to 1.[73] However, one should be cautious in calculating it because the anodic peak current (if the cathodic scan is started first) must be corrected to a zero current baseline to mitigate the disturbance of the capacitance effect at the interface.[73] For a Nernstian wave with a one-electron transfer, the difference of the two peak potentials should be 57 - 60 mV at room temperature.[71]

It is important to note that cyclic voltammetry may not be comprehensive to characterize some non-covalently anchored systems with strong surface interactions (e.g., axial coordination, π-π interactions) between the electrode and the molecular catalyst.[72] With such surface interactions, the Fermi level of the electrode strongly couples with the energy level of the redox center in the anchored system.[74] Therefore, there will be no potential drop between the electrode and the molecular catalyst, and no electron transfer will happen. In that case, cyclic voltammetry can only reflect the Faradaic reaction of the supporting electrolyte (**Figure 8b**).

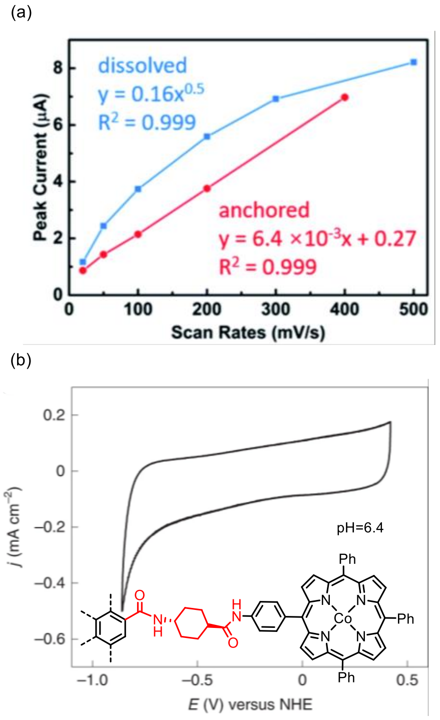

FIGURE 8. (a) Relationship between peak currents and scan rates for dissolved and anchored active species. Reproduced with permission from Ref. 49. Copyright 2021 The Royal Society of Chemistry. (b) CV trace of redox-active species strongly coupled with electrode surfaces. Reproduced with permission from Ref. 72. Copyright 2022 Nature Publishing Group.[49, 72]

2.3.2 Other useful techniques

To provide supplemental information besides cyclic voltammetry, spectroscopic techniques, including UV-Vis, IR spectroscopy, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS), are commonly engaged. For example, a triazole formed from azide-alkyne coupling has a representative band in IR spectroscopy, offering a unique feature to confirm the success of the immobilization. XPS provides the identification of elements that are present on the surface. UV-Vis and XAS are often combined to study the oxidation states of the metal center on the anchored site. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure analysis (EXAFS) are often employed to provide complementary structural information.

Additionally, many techniques allow an *in situ* mechanistic study by monitoring reaction processes (change in ν(CO) in CO_2 reduction, for example),[29] changes in oxidation state,[72] and shifts in bonding frequency and amplitude.[75] Finally, recent efforts on characterizing interfacial electric fields at electrode/electrolyte surfaces using vibrational sum frequency generation (VSFG) provide a good handle on understanding the electrified interface on a molecular level. A recent comprehensive review emphasized the potential of VSFG in exploring fingerprint bands of surface-adsorbed molecular species compared with other spectroscopic techniques.[70, 76] Surface-enhanced Raman spectroscopy (SERS) represents another powerful tool for *in situ* surface characterization with a well-elaborated example published recently.[77] To aid the interpretation of the surface-functionalized complex's performance, comparisons made between the immobilized and the homogenous species in solution using multiple techniques are highly valuable. Understanding the type of information provided by a specific method and taking advantage of those that offer complementary information allows a complete picture of the modified surface and its catalytic behavior.

3. ELECTROCATALYTIC REACTIONS RELATED TO ENERGY CONVERSION USING MOLECULARLY MODIFIED ELECTRODES

3.1 Electrocatalytic reactions by non-covalently functionalized moieties

Immobilized molecular electrocatalysis for energy conversion has been extensively studied.[20, 78] Taking CO_2 reduction as a model reaction, investigation of homogenous and heterogeneous electrocatalysts has been demonstrated.[4, 6, 7, 9, 18, 78, 79] We will start with a discussion on the effects on electron transfer and catalytic behavior caused by different linkages created from various types of immobilization methods along with examples of small molecule activation reactions such as oxygen evolution reactions (OER) and CO_2 reduction reactions.

3.1.1 Effects on electron transfer rate through different linkages

A comparison of covalent versus non-covalent immobilization of molecular species onto the electrode shows a significant difference in the electron transfer rate.[56, 80, 81] For example, covalently attached pyrene and 1-pyrenylferrocene on indium tin oxide (ITO) yielded pyrene-modified ITO (ITO|Pyr) and ferrocene-modified ITO (ITO|vinylferrocene), respectively.[56] To ITO|Pyr, the redox-active ferrocene was then physisorbed, resulting in non-covalently attached pyrenylferrocene on ITO|Pyr (ITO|Pyr|pyrenylferrocene, **Figure 9**). A kinetic study on electron transfer was performed on both ITO|Pyr|pyrenylferrocene and ITO|vinylferrocene. The electron transfer rate for the non-covalently modified system, ITO|Pyr|pyrenylferrocene, is about ten times faster than the covalently modified system ($k_{app} = 100 \pm 8\ s^{-1}$ compared to $9 \pm 2 s^{-1}$). Although the distance between the ferrocene moiety to the electrode seems shorter in ITO|vinylferrocene, the extent of π-conjugation of the linker was proposed to cause a faster electron transfer in the non-covalent immobilized system. However, opposite trend was found in recent study employing amino-substituted cobalt porphyrin to immobilize on carbon-based electrode.[80] Covalent grafted complex exhibits faster electron transfer rate and higher reactivity comparing to the non-covalently immobilized counterpart.

It is important to point out that the effects on electron transfer through different linkages depend on the electrode surface, molecule to immobilize, type of linkage, distance between the surface to the attached molecule, reaction/electron transfer mechanism, and so on. It is inexpedient to implicitly assume that non-covalent immobilization will result in faster electron transfer rate than covalent immobilization or vice versa. In fact, we will present studies indicating one immobilization method may surpass the other under specific circumstances for both cases.

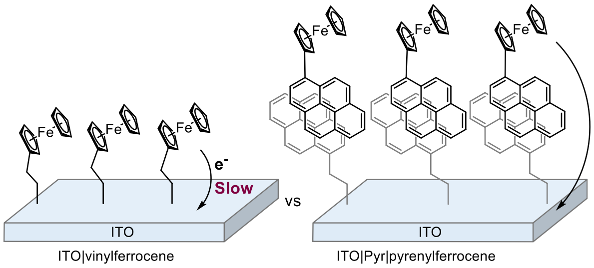

FIGURE 9. Interfacial electron transfer of ferrocene immobilized on ITO via covalent (left) and non-covalent (right) interactions.[56] Reproduced with permission from Ref. 56. Copyright 2018 American Chemical Society.

3.1.2 Enhancement of reactivity introduced by efficient electron transfer through immobilization

Efficient electron transfer between the electrode surface and an immobilized metal complex is necessary to accelerate a catalytic reaction, efficient electron transfer can introduce a boost in catalytic activity. Non-covalent immobilization of a molecular electrocatalyst was also applied in an oxygen reduction reaction and oxygen evolution reaction with a pyrene-modified cobalt complex (**Figure 10**).[82] High activity and durability were observed when a fluoro-substituted cobalt compound was immobilized on multi-walled carbon nanotubes. A four-electron reduction of oxygen to water in an acidic aqueous solution was achieved with an onset potential of 0.75 V *vs.* a normal hydrogen electrode (NHE). In comparison, water oxidation in a neutral aqueous solution was performed with an onset potential of 1.15 V *vs.* NHE. Compared to the molecular cobalt complex, an enhanced catalytic performance was observed, likely due to the strong π-π interactions between the catalyst and the electrode enabling efficient electron transfer for both reactions.

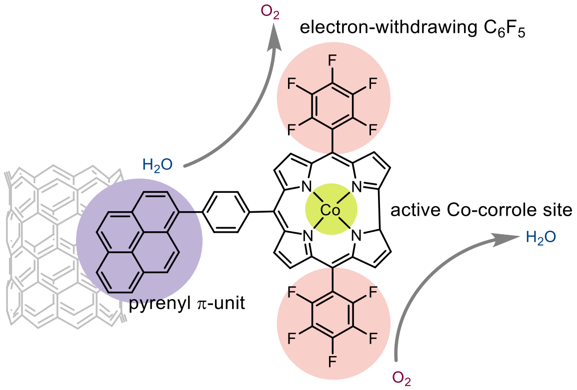

FIGURE 10. Non-covalently immobilized cobalt catalyst for oxygen reduction reaction and oxygen evolution reaction.[82] Reproduced with permission from Ref. 82. Copyright 2016 American Chemical Society.

3.1.3 Introducing new activity on the anchored complex through immobilization

In addition to enhancing the activity of a homogenous catalyst, immobilizing an organometallic compound on an electrode may induce new reactivity not observed in its non-immobilized analogue. For example, upon deposition onto a glassy carbon electrode, heterogenization of a cobalt naphthalocyanine complex onto doped graphene through π-π interactions resulted in up to 97% Faraday efficiency in CO_2 to CO reduction.[83] In contrast, the pristine cobalt complex on the electrode remained inactive toward CO_2 reduction. Based on elemental analysis and inductively coupled plasma (ICP) mass spectrometric measurements, S, N, and O atoms were doped on graphene to provide possible axial coordination sites to the cobalt center. Graphitic sulfoxide and carboxyl groups serving as extra binding sites for the cobalt complex were found to be efficient in strengthening the immobilization of cobalt (**Figure 11**). This is an inspiring example to utilize heteroatoms to provide extra interactions between the electrode and the metal center.

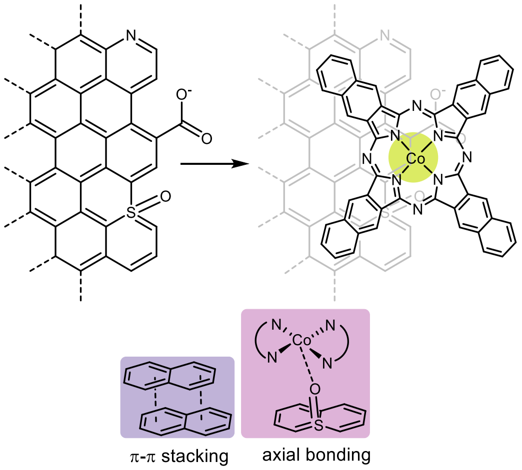

FIGURE 11. Immobilized cobalt naphthalocyanine via π-π stacking and axial bonding.[83] Reproduced with permission from Ref. 83. Copyright 2019 John Wiley & Sons, Inc.

3.1.4 Obtaining selectivity for different products via surface-attached metal catalyst

Selectivity is another critical factor to consider when assessing a molecular catalyst. Catalyst that produces one product over the other selectively enables a good control of the reaction outcome. An established strategy to implement selectivity on a catalyst in a homogenous system is to modulate the supporting ligand. In a heterogenized system, tuning the selectivity of products can be achieved by modifying the surface loading of the metal complex. An example of selective production of CO over formate in CO_2 reduction was demonstrated with a carbon nanotube electrode surface functionalized with a Mn(bipyridine)-pyrene complex (**Figure 12**).[29] The molecular species was immobilized via π-π interactions between the pyrene moiety of the Mn complex and the electrode. The successful immobilization was confirmed electrochemically and spectroscopically. The hybrid electrode showed high activity for CO_2 reduction with turnover numbers (TONs) up to 1790 ± 290 for CO and 3920 ± 230 for formate at an applied potential of −1.1 V *vs.* standard hydrogen electrode (SHE). The selectivity was tuned by controlling the surface loading of the molecular catalyst. A Mn hydride was responsible for converting CO2 to formate at low catalyst loading. In contrast, at high loading, a Mn dimer intermediate was proposed after reduction, leading to the production of CO.[29] Catalytically active species were identified by *in situ* UV-vis and attenuated total reflectance infrared spectroscopy (ATR-IR). These results showcase the possibility of achieving selectivity with an electrode surface-attached metal complex catalyst. However, the rate for CO_2 reduction decreased due to the deactivation of the immobilized Mn electrocatalyst after a few hours while the rate for H_2 evolution was less influenced. Therefore, challenges remain on increasing stability and durability of the designed immobilized system.

3.2 Electrocatalytic reactions by covalently functionalized moieties

A typical design of a molecularly modified electrode, as discussed in **Section 2**, often starts with an optimized molecular catalyst for a specific type of reaction with an electrode support as the electron source.[72] However, the logic of such a design lies in the assumption that the activity of the molecular catalyst translates invariably after heterogenization. In **Section 3.1**, we described the impact on the activity of the immobilized molecular catalyst. Studies have shown that the immobilization method dramatically affects the reactivity of the resulting system. Here we will include cases studying covalent linkage effects on electron transfer, reactivity, and reaction mechanism of the appended molecular catalyst on energy conversion reactions. It is essential to realize the significance of electron transfer on the modified surface in electrocatalysis.[26] In the previous example shown in **Figure 9**, an intermolecular electron transfer (from the electrode to ferrocene) was observed at different rates depending on the distance between the electrode and the redox-active species for non-covalent immobilization.[56] In addition, the efficiency of electron transfer is found to be affected by the conjugation degree of the tether.[83] In an extreme example involving full conjugation between the electrode and the chemical modification, a concerted proton-electron transfer pathway typically observed for metal electrode surfaces was achieved.[67, 84] This observation is contrary to the well-known stepwise mechanism of molecular electrocatalysis, where electron transfer and substrate activation are separated. A detailed study by Surendranath and coworkers demonstrated that such mechanistic changes could be obtained by strong electronic coupling between the immobilized molecule and the electrode and could be affected by changing solvents.[72, 85] In the following section, we will start with a general introduction of the strategy to form strongly coupled linkages with examples demonstrating subsequent effects on electron transfer and catalytic activity. We will discuss the mechanistic changes by comparing strongly coupled and weakly coupled linkages. Lastly, we include covalent linkages commonly employed involving electrografting and "click" reactions along with the benefits of enhancing catalytic activity and improving catalyst lifetime.

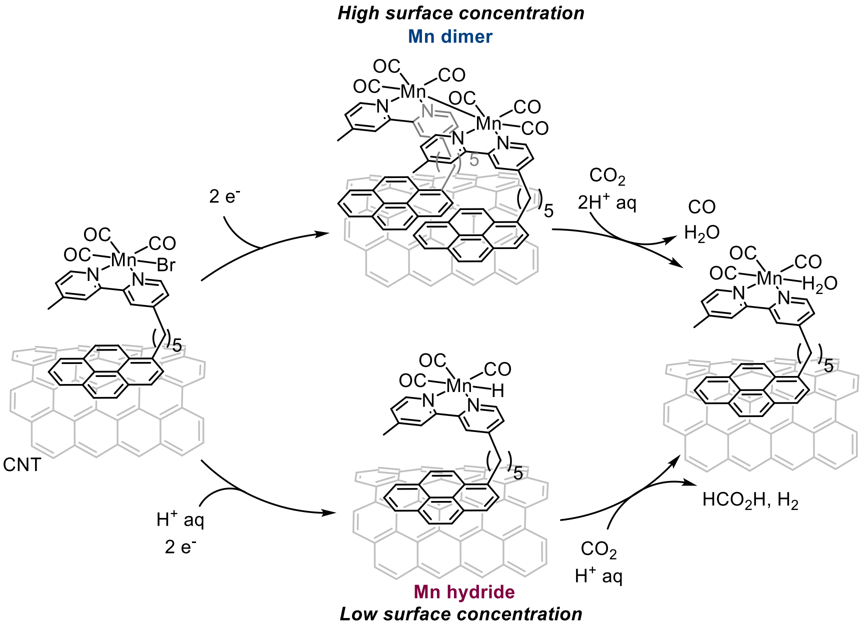

FIGURE 12. Non-covalently immobilized Mn complex selectively produces CO and formate from CO_2 reduction.[29] Reproduced from Ref. 29. Copyright 2017 American Chemical Society.

3.2.1 Strong coupling between the electrode surface and the attached metal complex through full conjugation

To gain a deeper insight into the electronic coupling between molecules conjugated to the graphitic surface of the electrode, a series of graphite-conjugated organic/organometallic complexes was investigated. Graphite conjugation through amine-quinone condensation induces a strong electronic coupling between the functionalized moiety to the electrode, resulting in a fundamentally different electron transfer behavior for graphite-conjugated catalysts compared to their homogeneous counterpart in electrochemical reactions (**Figure 13**).[67] In short, graphite-conjugated catalysts behave more "electrode-like" than "molecule-like." Different from molecular electrocatalysis, where a redox event is separated from substrate activation, the strong coupling introduced by the conjugated linkage between the electrode and immobilized metal complex induces a concerted electron transfer pathway and eliminates redox intermediates.[84] Furthermore, the oxidation state of the transition metal center on the site remains unchanged under electron transfer conditions. Coupling the molecular moiety to the electrode offers a better stabilization of excess charges through delocalization. The molecular catalyst may not undergo the exact mechanism compared to its homogenous state. When a potential is applied to the electrode, the homogenous catalyst experiences a change in the electric field that changes the driving force of electron transfer. However, the difference between the Fermi level and the redox potential of the molecule remains unchanged after immobilization. Therefore, the driving force remains the same. Instead, electron transfer only occurs when coupled with ion transfer under an applied potential. The delocalization of electrons in the electrode prohibits the oxidation state of the metal center. Together, graphite conjugation allows tuning heterogenized electrocatalysis at the molecular level by providing an alternative to obtaining a precisely controlled catalyst with an optimal reaction rate and electron efficiency.[7, 84]

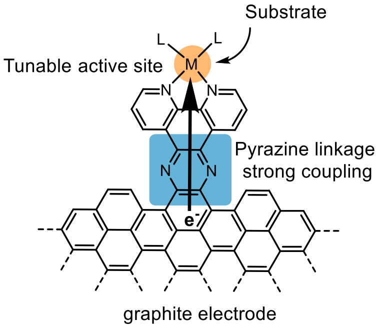

FIGURE 13. Strong electronic coupling through a conjugated linkage.[67] Reproduced with permission from Ref. 67. Copyright 2018 American Chemical Society.

Employing graphite-conjugated catalysts in CO_2 reduction demonstrates a possible application in energy conversion reactions with increased stability of the electrocatalyst.[64] *fac*-Re(5,6-diamino-1,10-phenanthroline)$(CO)_3Cl$ covalently conjugated to graphite resulted in a graphite-conjugated rhenium material that was highly active in the CO_2 to CO reduction in acetonitrile (**Figure 14**).[64] The graphite-conjugated Re catalyst displayed 96 ± 3 % Faradaic efficiency and turnover numbers greater than 12,000. The cyclic voltammogram of the graphite-conjugated rhenium material, recorded under catalytic conditions (CO_2-saturated acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate electrolyte), displayed a catalytic current at 10 mA cm^{-2} at -2.09 V with CO as the only product. Covalent conjugation of rhenium onto the glassy carbon electrode increased the stability of the compound compared to adsorption or electropolymerization methods. The graphite-conjugated Re catalyst remained robust for 1.4 ± 0.3 h with a sustained catalytic activity at 1.0 mA. An enhanced activity compared to the homogenous analogue, high selectivity for CO, and extended durability of the catalyst were observed.

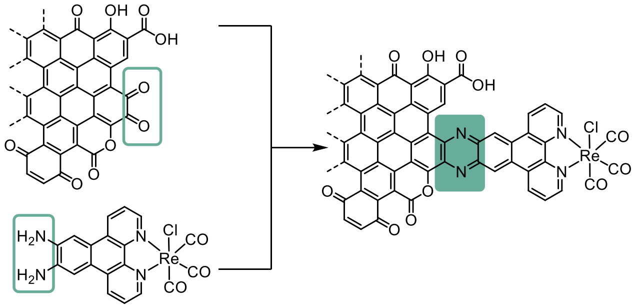

FIGURE 14. Graphite-conjugated rhenium active site for CO$_2$ reduction.[64] Reproduced with permission from Ref. 64. Copyright 2016 American Chemical Society.

Graphite-conjugated pyrazines obtained from the same condensation method displayed high activity in oxygen reduction, which was not observed for the molecular analogues of pyrazines.[86] The catalytic activity of graphite-conjugated pyrazines for oxygen reduction in an alkaline aqueous electrolyte can be controlled by changing the electrophilicity of pyrazines. Although unmodified glassy carbon electrodes showed activity in oxygen reduction at 0.6 V, graphite-conjugated pyrazines displayed a much higher current at the same voltage, suggesting they were better catalysts under the same conditions. However, the surface site density of electroactive pyrazines, ranging from 14 to 250 pmol cm^{-2}, was relatively low. Tafel studies revealed that the difference in activity in oxygen reduction catalyzed by graphite-conjugated pyrazines could be easily tuned by modifying the substituents on pyrazines. An increased turnover frequency was observed by switching from methyl (0.12 ± 0.01 s^{-1}) to a more electron-withdrawing fluoro-substituted graphite-conjugated pyrazine (0.35 ± 0.01 s^{-1}) as depicted in **Figure 15**. In a later study, a stepwise mechanism in which a proton-decoupled oxygen activation involves an electron transfer along with oxygen adsorption at the conjugated pyrazine surface, followed by several electron/proton transfers, was proposed.[87] This example further proved that the covalent conjugation of pyrazines on glassy carbon electrodes is an opportunity to combine the advantages of homogenous and heterogeneous catalysis. The catalytic activity of graphite-conjugated pyrazines can be easily adjusted by modifying the electronic properties of the molecular attachments on the active site. Secondly, efficient electron transfer and a higher catalytic rate can be achieved only in the hybrid system, suggesting that reactivity that was not observed for molecular analogues can be introduced through molecule-electrode derivatization.

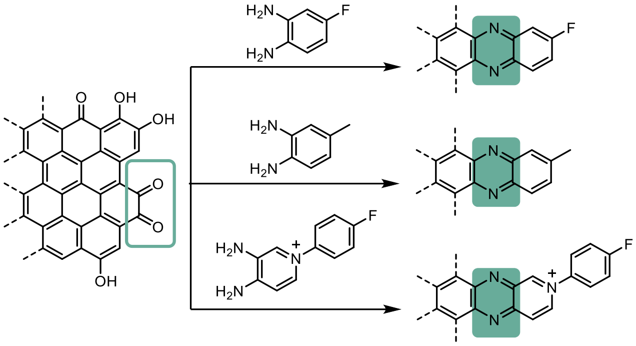

FIGURE 15. Condensation of *o*-phenylenediamine derivatives with the *o*-quinone edge sites of graphene sheets to generate graphite-conjugated pyrazines.[86] Reproduced with permission from Ref. 86. Copyright 2015 American Chemical Society.

3.2.2 Comparison between strong coupling through conjugation and weak coupling via an amide linkage

A detailed mechanistic investigation was performed on the graphite-conjugated cobalt tetraphenylporphyrin (GCC-CoTPP) and non-conjugated cobalt porphyrin complex (Amide-CoTPP).[65] In the first paper reported by Kaminsky *et al.*, a dramatic enhancement in the rate of oxygen reduction reaction was observed through strong conjugation on GCC-CoTPP compared to the low/non-conjugated Amide-CoTPP (**Figure 16**).[65] Although both GCC-CoTPP and Amide-CoTPP can catalyze oxygen reduction reactions, Amide-CoTPP displayed an onset current density of 10 μA cm^{-2} at 0.66 V, whereas GCC-CoTPP displayed the same onset current at 0.72 V, revealing almost an order of magnitude improvement in turn over frequency. The strong electronic coupling provided by the highly conjugated pyrazine linkage enabled rapid electron transfer which significantly enhanced the rate of oxygen reduction.

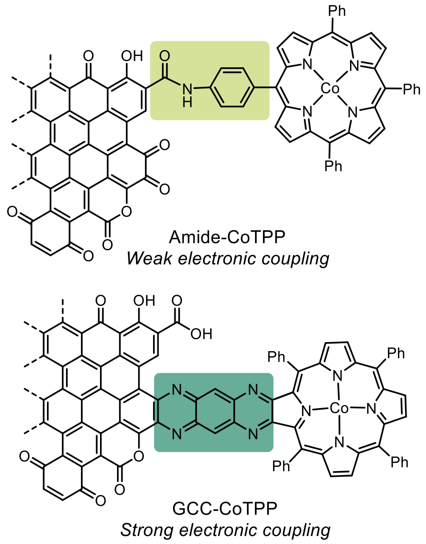

FIGURE 16. Immobilization of cobalt porphyrin onto modified electrode surface through an amide and conjugated pyrazine linkage.[65] Reproduced with permission from Ref. 65. Copyright 2019 American Chemical Society.

Building on this work, the same group proposed another way to enforce a concerted mechanism for the weakly conjugated amide-linked cobalt catalyst. Chemically modified electrodes derived from the covalent anchoring strategy through an amide linkage are supposed to adopt a stepwise and redox-mediated reaction pathway during electrocatalysis.[73] The metal centers reach their active states by gaining or losing electrons from the electron flow through the electrostatic potential gradient within the electrical double layer. The electron transfer process is then followed by chemical reactions of the substrates at these active metal sites in the electrolyte. However, this commonly adopted redox mediation mechanism does not hold in the case of solid surface coupling in previous studies on graphite conjugated catalysts which on the contrary, adopted the concerted pathway. Interestingly, although the amide linkage was considered to provide weak coupling compared to the pyrazine linkage, it could undergo a concerted pathway based on the choice of solvent.[72]

To understand the requirements for a surface-attached metal complex to behave like a metal electrode versus a molecular catalyst (serve as a redox mediator), a glassy carbon electrode surface-attached cobalt complex in different solvent systems was investigated (**Figure 17a**). In this work, the authors utilized an aliphatic tether to anchor a cobalt porphyrin on the surface of a pre-oxidized glassy carbon electrode. In acetonitrile, an outer-sphere electron transfer corresponding to the $Co^{II/I}$ redox event was observed, consistent with the analogous homogenous system. The hybrid system was found to be catalytically active in catalyzing hydrogen evolution reactions via a stepwise pathway, which is commonly adapted by molecular catalysts. In contrast, no cobalt-based redox event was observed by cyclic voltammetry in aqueous media with various pH values. The key difference between the molecularly modified electrode in the two systems is that in acetonitrile, the homogenous analogue and the anchored catalyst remained soluble and thus are considered freely solvated and stay outside the double layer. In contrast, the molecular cobalt complex and the anchored catalyst remained insoluble in the aqueous solution and were forced to stay close to the electrode within the double layer (**Figure 17b**) due to extra surface interactions (axial coordination and π-π interactions, **Figure 17c**). Therefore, the redox potential of cobalt porphyrin will depend on the change of the Fermi level of the carbon electrode modulated by the external potentiostat. No electron transfer to the cobalt center can happen due to the lack of potential drop between the carbon electrode and covalently anchored cobalt porphyrin. However, hydrogen evolution reactions can still proceed in aqueous media with their proposed concerted proton-electron transfer mechanism. Under the circumstance, a proton could travel across the electrical double layer and bind to the cobalt center because of the electrostatic potential difference between the active cobalt sites and the bulk electrolyte. At the same time, the abovementioned strong surface interactions can enable electron flow within the same time scale of proton transfer and binding. This hydrogen evolution reaction enabled by the concerted pathway involving proton binding and electron transfer made the chemically modified glassy carbon electrode act like a metallic electrode and distinct from the redox-mediated reaction pathway in organic media or its soluble analogue.

This study raises a salient point in designing a molecularly modified electrode: besides selecting a highly active molecular complex and developing a heterogenization method, a fundamental understanding of the reaction mechanism and possible solvent effects should be considered. The mechanistic changes in the same reaction for the same modified electrode in a different solvent system are attributed to the electrostatic coupling between the molecule and the surface.[72] The intrinsic redox feature of the molecular compound may not always be detected after immobilization if there are no substrates, despite the minimal effect of structural modifications to enable immobilization. In the present study, the strong electrostatic coupling of the anchored metal complex was the key component that caused a dramatic change in the mechanism. It is important to note that the flexible amide linkage plays an essential role in allowing both solvation and surface adsorption to be possible in a single system. In other words, the performance of a heterogenized system is influenced by multiple factors: the molecular analogue, the linkage enabling immobilization, the solvent, and so on, which poses challenges in this exciting frontier.

3.2.3 Electro-grafting provides alternative covalent linkage with enhanced catalytic activity

The highly conjugated linkage between a molecular moiety and an electrode often involves a specific type of functional group (e.g., *o*-quinone) that requires pretreating the electrode and leads to a low catalyst loading. Immobilizing metalloporphyrins onto a conductive oxide support via grafting illustrates yet another possibility towards catalytic activity enhancement.[88] Electrodes composed of nanostructured indium tin oxide (nanoITO) were prepared either by direct grafting of a cobalt porphyrin complex forming CoP|nanoITO or grafting a layer of poly(vinylpyrindine) followed by coordination to the cobalt center through the pyridine group forming CoTPP|PVP|nanoITO (**Figure 18**). With ITO as the supporting electrode, the metal center was responsible for the redox process. A cyclic voltammetry study of CoP|nanoITO electrodes displayed two one-electron redox processes corresponding to $Co^{III/II}$ and $Co^{II/I}$ at a half potential $E_{1/2}$ of 0.15 and -1.19 V vs. Fc^+/Fc. In contrast, under the same conditions, redox events at -0.2 and -1.34 V vs. Fc^+/Fc were observed for CoTPP|PVP|nanoITO. These redox potential shifts represent a direct manipulation of the electrochemical property of the hybridized electrocatalyst by changing the interaction between the electrode and the molecular species. However, controlling the number of cobalt complexes that can be coordinated to the polymer chain remains challenging. Possible non-covalent interactions of the porphyrin ligand with the electrode surface, as well as metal complexes coordinated to the pyridine unit that is too far away from the electrode, may complicate the system.

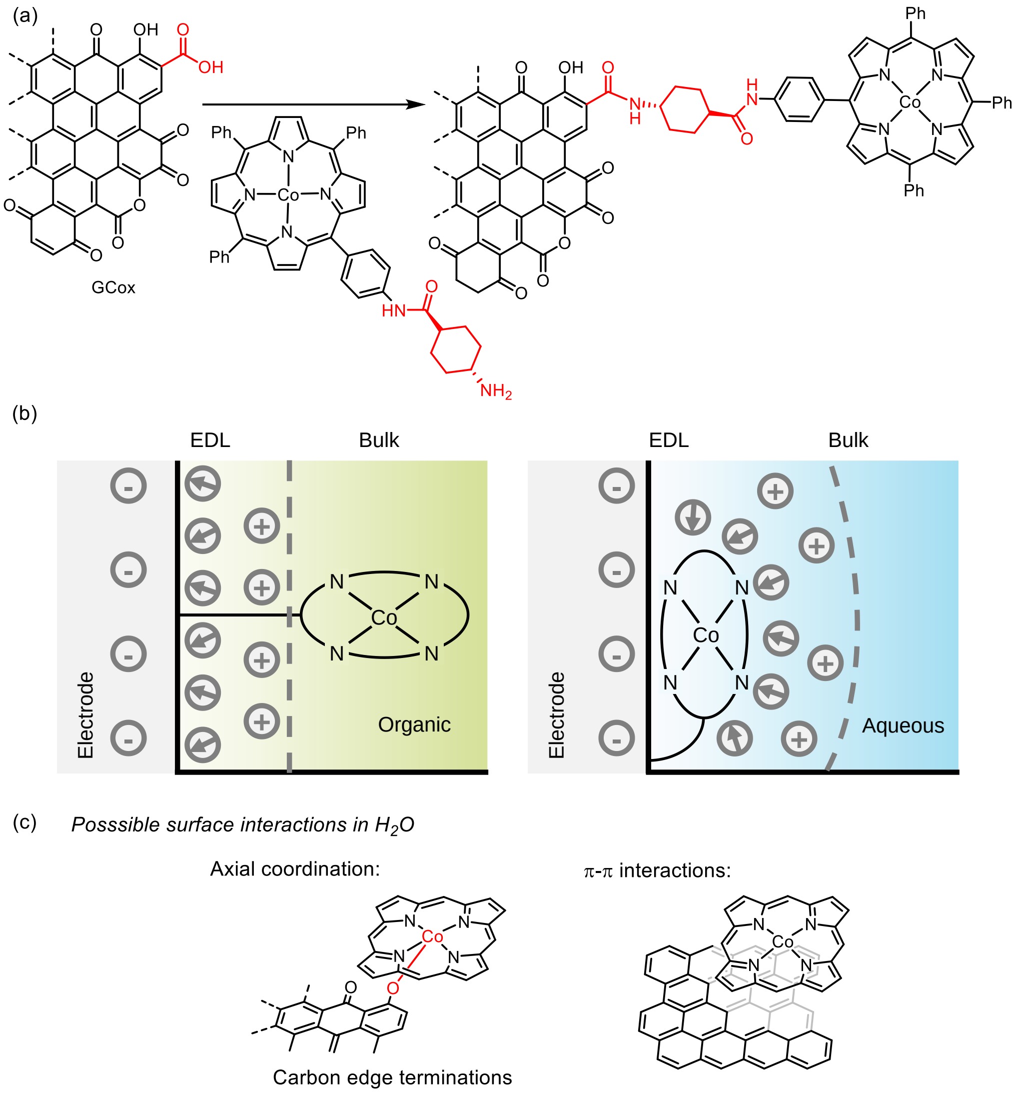

FIGURE 17. (a) Chemically anchored cobalt porphyrin with an aliphatic tether on the surface of a pre-oxidized glassy carbon electrode; (b) Interfacial environment of the electrode with chemically anchored cobalt porphyrin in an organic (left) and aqueous (right) electrolyte; (c) Possible non-covalent interactions between cobalt porphyrin and electrode in an aqueous electrolyte.[72] Reproduced with permission from Ref. 72. Copyright 2022 Nature Publishing Group.

Covalent immobilization via diazonium grafting is also widely applied in preparing immobilized molecular electrocatalysts.[89-91] Covalently grafted Ir complexes onto carbon electrodes achieved a turnover frequency of up to 3.3 s^{-1} and a turnover number of 644 during the first hour of electrochemical water oxidation reaction (**Figure 19**).[92] However, there was a minor loss of carbon material on the electrode surface, decreasing the catalytic activity. Nevertheless, enhanced activity was observed compared to the molecular analogue. Encouraged by the incredible behavior of the grafted carbon-based electrode in water oxidation reactions, various metal complexes including Mn porphyrin were investigated applying the same immobilization strategy. Both covalently and non-covalently immobilized Mn porphyrin complexes were employed in water oxidation and oxygen reduction reactions.[93] Covalent ligation of the Mn complex onto a carbon electrode through electroreduction of a porphyrin diazonium salt followed by metalation and electrodeposition yielded an electrochemically active catalyst with a controllable amount of active sites. The immobilized catalyst reached an overall catalytic current for the oxygen reduction reaction 2.4 times higher than that of the non-covalently anchored catalyst. The proposed explanation for the improvement was due to the shorter average Mn-Mn distance, which enabled the simultaneous participation of two metals (**Figure 20**). Note that changing the electrodeposition time, therefore changing the concentration of Mn active sites on the electrode surface, allowed two metal centers to participate in the 4-electron process.

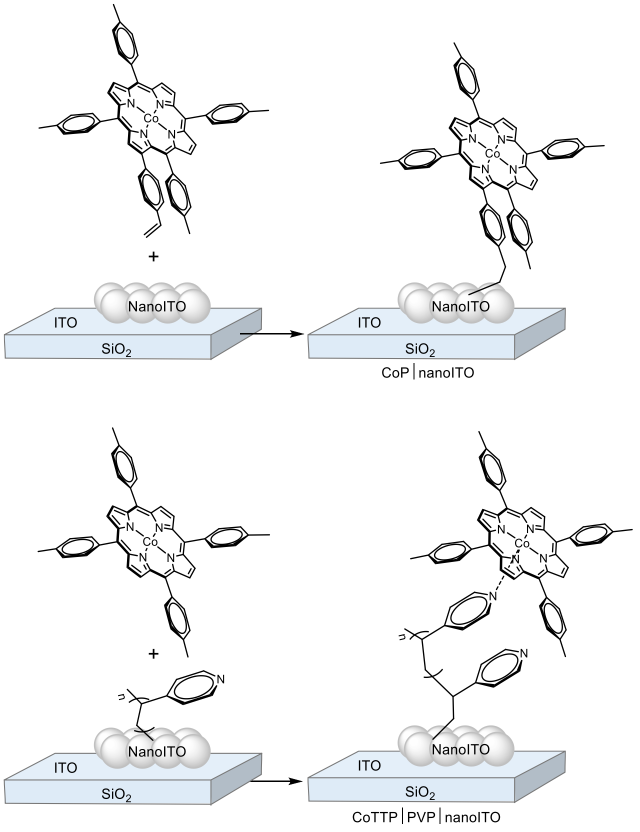

FIGURE 18. Depiction of strategies used to assemble a molecularly modified ITO electrode.[88] Reproduced with permission from Ref. 88. Copyright 2020 American Chemical Society.

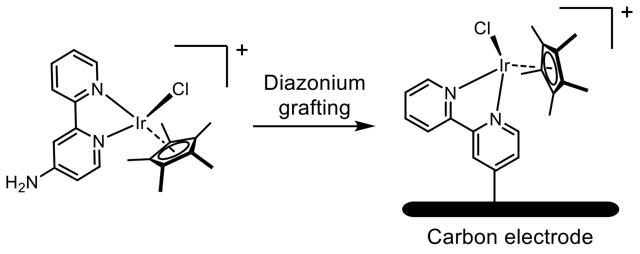

FIGURE 19. Immobilization of iridium complex via diazonium grafting.[92] Reproduced with permission from Ref. 92. Copyright 2012 American Chemical Society.

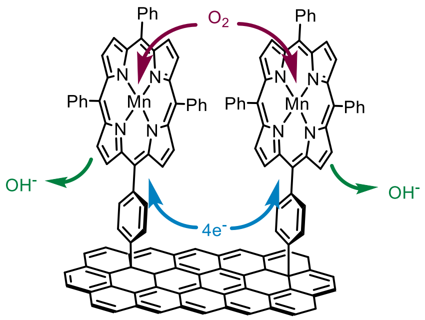

FIGURE 20. Manganese complex grafted on carbon electrode for oxygen reduction reaction.[93] Reproduced with permission from Ref. 93. Copyright 2019 American Chemical Society.

3.2.4 Covalent linkage via click reactions improves catalyst lifetime and catalytic activity

Anchoring a cobalt complex onto a doped conductive diamond electrode through azide-alkyne cycloaddition demonstrates another elegant way to employ an organometallic complex-modified electrode with good stability and activity in CO_2 reduction.[66] The photochemical grafting method created an sp^3-sp^3 C-C linkage between the electrode surface and attached the cobalt complex via a "click" reaction (**Figure 21**). The onset of catalytic current was observed at -1.93 V *vs.* Fc/Fc$^+$ and remained unchanged after 1000 cycles. The same immobilization strategy can be applied to other metal complexes.[94] For example, $[Fe_4N(CO)_{12}]^-$ was immobilized on a glassy carbon electrode via a "click" reaction which exhibited reactivity at -1.2 V *vs.* SCE for the production of formate in an aqueous solution. The iron complex modified electrode survived three days of testing, showing a significantly improved electrocatalyst stability.

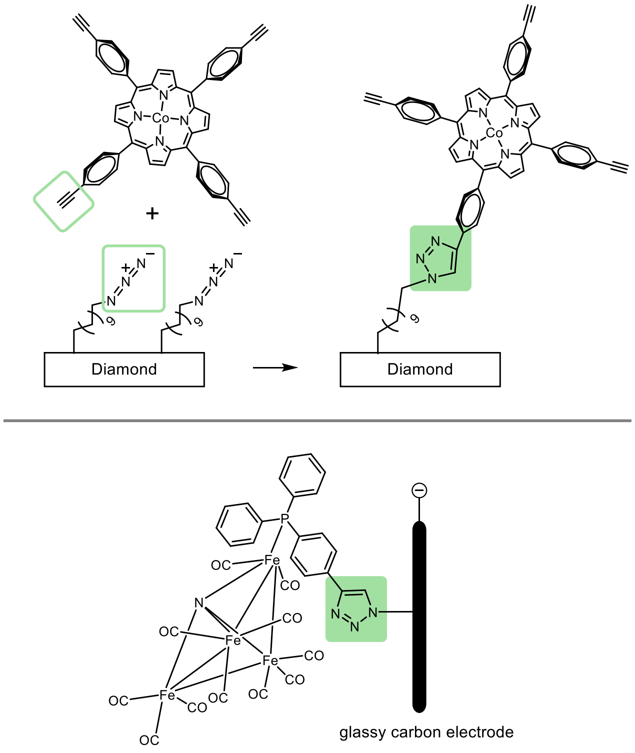

FIGURE 21. Covalent immobilization using a "click" reaction for a cobalt complex (top, Reproduced with permission from Ref. 66. Copyright 2012 American Chemical Society)[66] and iron complex (bottom, Reproduced with permission from Ref. 94. Copyright 2019 American Chemical Society).[94]

Examples of CO_2 reduction, oxygen evolution and reduction show that immobilization generally introduces a high activity to the molecular electrocatalyst due to a facile and efficient electron transfer from the electrode support to the catalyst through covalent or non-covalent interactions. A highly conjugated molecular linker also results in a strong electron coupling between the molecular moiety and the electrode than other methods. However, non-covalent interactions such as π-π stacking, depending on the catalytic system, may still exhibit higher activity than covalently ligated analogues. A comparison between a short conjugated linker, a long alkene linker, π-π interactions, and simple adsorption of cobalt complexes on carbon nanotubes in electrocatalytic water splitting reveals that the short conjugated linkage surpasses π-π interactions and the long alkene linker in electron transfer ability.[95] In addition, those three immobilization methods afford a stable catalytic material, which could stabilize active intermediates during the reaction and showcase a long lifetime with minimal catalyst aggregation.

It is worth noting that the distance between the catalytically active center to the electron source is crucial in determining activity. The effective range of diffusion for the immobilized molecular electrocatalyst (considering the coordination and solvation of the reactants) is on the order of tens of nanometers, thus, the length of the linkage is also an essential factor to consider when designing an immobilized system.[79] Debates on whether the influence of the immobilized molecule is either through structure or through space are still ongoing. In the previous examples of strongly coupled graphite conjugated catalysts and weakly coupled amide-linked catalysts, we discussed that choosing the solvent in which the homogenous analogue of the anchored catalyst is soluble could enforce the weakly coupled electrode-catalyst complex to undergo a concerted pathway. Thus, the nature of bonding/linkage between the electrode and the molecular modification is not the sole factor that determines the catalytic activity. Electrostatic interactions between the immobilized molecule and the electrode play a crucial role.

4. CATALYSIS CONTROLLED BY ELECTROSTATIC INTERACTIONS

4.1 Electrostatic interaction induced by applying an electric potential

In the previous section, we discussed the importance of considering electrostatic interactions in an electrocatalytical system of molecularly modified electrodes. Being aware that electrocatalysis is initiated by applying current, the effects of electric fields must be considered as well.[75, 96-99] External electric fields are a general term referring to the uniform electric field generated by a voltage bias.[100] Aligning an electric field along a specific bond axis can either elongate or shorten the bond.[101] By precisely controlling the orientation of an external electric field along a reaction axis (the direction of bond breaking and bond-forming), a reaction can be accelerated or slowed down.[100, 101] Thus, the orientation of the electric field is crucial in catalysis. Additionally, an electrostatic field-induced stabilization of the transition state can lower an activation barrier.[102] An oriented external electric field is an external electric field that is oriented to a specific direction and can be generated by a dipolar field, scanning tunneling microscopy (STM), and charged surfaces in electric cells.[100] Contrary to electrocatalysis, where electrons are gained or lost associated with current applied to promote electrochemical reactions, the electrostatic field exists in charged functional groups and surface, solvent, and electrolytes.[103] A general strategy involving oriented external electric fields in catalysis on the atomic scale is represented by single-molecule experiments via STM.[8, 104-106] Detailed discussions on theoretical and experimental studies on external electric fields and oriented external electric fields have been elaborated in recent reviews.[100, 102, 103, 106-108] However, harnessing oriented external electric fields by STM has limitations on scalability. As an alternative, the interfacial design of electric cells has been developed to demonstrate the possible application of electrostatic field in catalysis. Herein, we would like to emphasize the significance of electrostatic field resulting from an external voltage applied in an electric cell, and discuss its effects on the catalytic system. We refer to the catalytic system enabled by electrostatic field "electrostatic catalysis" to differentiate from electrocatalysis enabled by electric current. We will focus on interfacial experiments to discuss the potential role of immobilized electrode surfaces.

4.1.1 Catalytic activity of a molecularly modified electrode surface upon applying potential

An electric field exists in electrical cells responding to potential differences. In non-Faradaic electrochemical cells (no current), interfacial electric fields exist near the surface of charged electrodes where ions gather around and create a double layer in response to an electric field.[100] An electrode surface under the condition of gaining or losing electrons establishes a potential difference concerning the bulk solution.[102] A double layer of charges is created by responding to the compensated ion movement. The magnitude of oriented external electric field can range from 0.3 to 1.0 V $Å^{-1}$, and the interfacial electric field on an electrode surface ranges from 0.01 to 0.1 V $Å^{-1}$.[100] Understanding the cause of the electrostatic field and possibly quantifying it in an electrochemical cell could be beneficial for optimal catalytic activity.

Surendranath and coworkers reported on quantifying interfacial electric fields at the Pt/H_2O interface for the hydrogenation of 2-butene-1,4-diol at different pH values and across a wide range of ionic strength of the electrolyte.[96] However, only a few examples in this field involved molecularly modified electrodes and discussed their role in the electrostatic field for catalysis. Nonetheless, an organic functionality was employed to investigate the catalytic activity of a modified system in the presence of an electric field. Electric-field-assisted anion-π catalysis was studied, exploring the addition of a malonic acid half thioester to enolates in the presence of immobilized catalysts on a conductive ITO surface (**Figure 22**).[109] Applying a positive potential to the surface to increase the polarization of the catalyst and the recognition of anionic intermediates stabilized the transition state for the disfavored addition product.[110, 111] Therefore, an inversion of selectivity toward the unfavored product **A** shown in **Figure 22** was observed when increasing the electric field. The electric field polarized the modified surface and stabilized the corresponding transition state, leading to the formation of the desired product.

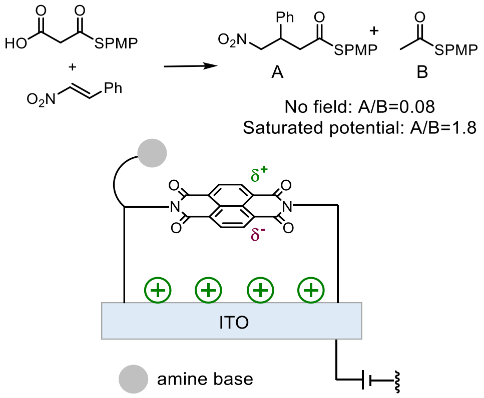

FIGURE 22. Anion-π catalysis assisted by electric field.[109] Reproduced with permission from Ref. 109. Copyright 2017 American Chemical Society.

4.1.2 Evaluating the effect of the electrostatic field on catalytic activity using a parallel plate cell

Efforts toward controlling the selectivity of chemical syntheses have focused on modifying the molecular structure of chemical components in the system. Identifying the effective structural feature and making desired modifications require tremendous work. Alternatively, we discussed that an external electric field could alter reaction selectivity by inducing field-dipole interactions. However, applying large electric fields to reactions and studying their effects remains challenging.[112] Kanan and coworkers developed a parallel plate cell, which allows the application of a large electric field to the system, to evaluate the electric field-induced change in selectivity in an Al_2O_3-catalyzed epoxide rearrangement (**Figure 23**).[112] In this study, depositing a thin layer of Al_2O_3 on a p-doped Si electrode was obtained, and the electrode surface after modification was considered catalytically active. Al_2O_3 coated on the electrode with alkylphosphonic acid was used as a counter electrode. Applying a voltage between the two electrodes generated an electrochemical double layer where the placement of ionic and polar molecules was controlled by the interfacial electric fields at each electrode-electrolyte interface. An increasing ratio of aldehyde to ketone was observed when the applied potential was less than -3 V and more than 3 V compared to no potential applied. It was also found that changing the type of phosphonic acid coating on the counter electrode affected the capacitance of the cell and further led to the changing of the electric field strength. Up to a 10-fold increase in the ratio of the two products was observed. Furthermore, the electric field was influenced by solvents, resulting in a dramatic change in selectivity. In CH_2Cl_2, up to a 63-fold enhancement was observed compared to CH_3CN. This study represents a proof-of-concept that the use of a parallel plate cell provides an alternative method for engaging interfacial electric fields on a relatively large scale for selective transformations. The use of an insulating coating decouples electrostatic from the electrochemical effects. Thus, the change in selectivity solely resulted from the change in electric potential, showing the irreplaceable role of the interfacial electric field.

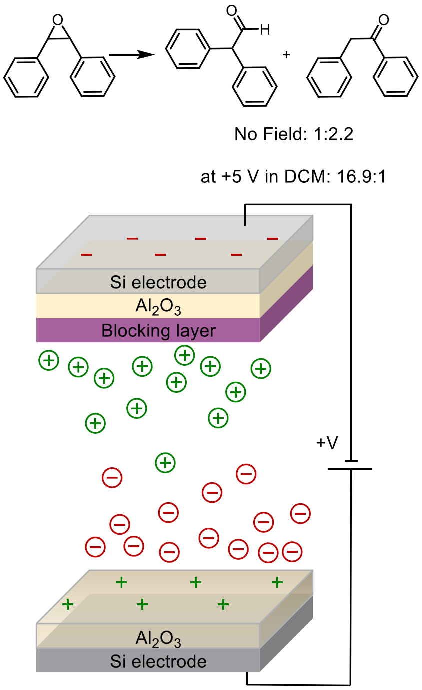

FIGURE 23. Selectivity in epoxide rearrangement achieved by the electric field in a parallel plate cell.[112] Reproduced with permission from Ref. 112. Copyright 2012 American Chemical Society.

Taking advantage of the ingenious design of the parallel plate cell, the same group expanded their study on carbene rearrangement reactions catalyzed by adsorbed and immobilized rhodium catalysts in the presence of an interfacial electric field (**Figure 24**).[113] Adapting a similar design as the previous study, Si electrodes coated with metal oxide layers were used as the opposing plates with rhodium porphyrin catalyst in between the dielectric-electrolyte interface. Applying voltage to the parallel plate cell resulted in changes between the cyclopropanation product C and insertion product D of the carbene rearrangement reaction. In the absence of an applied voltage, the Rh-catalyzed intramolecular carbene reaction from diazoketone formed products C:D in an approximate ratio of 10:1. Upon applying a voltage, the surface coating affected the ratio: the covalently attached Rh catalyst via the phosphonate-oxide linkage on the TiO_2 surface with a higher dielectric constant was observed to induce an increase in the ratio up to >100:1 at +4 V as a result of increasing charge density, indicating an almost absolute selectivity toward **C**; on the contrary, the Al_2O_3 or alkylphosphonate coated surface caused a decrease of the ratio. Such a decrease in the C:D ratio was observed for Al_2O_3-coated surfaces regardless of the positive or negative voltage applied. A comparison between covalently attached versus surface adsorbed Rh catalysts was conducted with a similar trend in selectivity change observed: both covalently immobilized and physically absorbed Rh complex on Al_2O_3 coated surfaces caused a decrease in the ratio, whereas on painted TiO_2 surfaces, an increase in the ratio was found. Specifically, the covalently attached Rh complex on the Al_2O_3 surface decreased the ratio of **C**: **D** to 6.3:1 at -5 V. In comparison, the ratio dropped to 1.6:1 at +5 V in the case of the absorbed Rh complex on the Al_2O_3 surface. Results obtained from the adsorbed Rh on TiO_2/Si surface resembled that of the covalently immobilized Rh. This study demonstrates a successful control of selectivity of a Rh-catalyzed intramolecular carbene reaction otherwise challenging to achieve. It is essential to highlight the effect of the solid surface selected for such a study: the direction of the selectivity change was a direct result of the dielectric property of the surface, as observed from the difference in Al_2O_3 versus TiO_2. Either with or without covalent linkage, the Rh complex was found to localize at the dielectric-electrolyte interface, representing an exciting avenue to exploit.

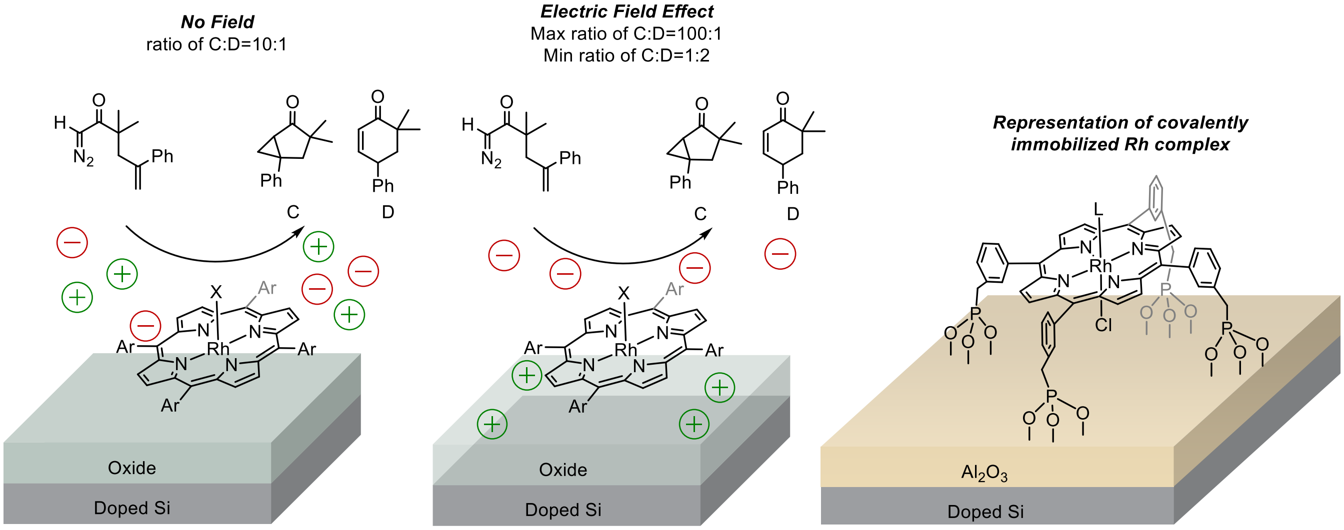

FIGURE 24. Change in product ratio induced by the electric field for rhodium-catalyzed cyclopropanation reaction (L, ligand).[113] Reproduced with permission from Ref. 113. Copyright 2013 American Chemical Society.

4.2 Investigating electric field and electrostatic interaction in an electric cell for redox reactions

In Section 3.2, the implications of solvation of the immobilized moiety in an electrochemical redox reaction were discussed. The preference for solvation of the surface-attached cobalt complex in acetonitrile caused it to stay outside the electron double layer, where an outer-sphere, redox-mediated, stepwise mechanism for hydrogen evolution reaction occurs. On the contrary, poor solvation of the same immobilized catalyst in an aqueous electrolyte forced it to stay within the double layer and be stabilized by additional interactions with the surface (axial coordination and π-π stacking).[72] As a result, a disparate reaction mechanism bypassing redox-mediation was observed (**Figure 25**). In the previous section, we discussed the investigation of electric field-induced electrostatic interaction in an insulated cell for non-redox reactions and emphasized the uniqueness and advantages of the parallel plate cell design. However, it is also imperative to understand the impact of local electric fields in an electric cell where a continuous current is supplied to catalyze electrochemical transformations.[107] For instance, alkali metals can increase the accumulation of CO_2 at the electrode, therefore, facilitate the reduction rate by increasing the local concentration of CO_2.[107, 114] The electric field generated by ions/charges is proven to stabilize key intermediates in the transformation as well.[115] Those findings suggest a different angle of viewing the implication of the molecular structure (ligand + substituents) when designing a chemically modified electrode for electrochemical reactions: instead of focusing on the change of the redox potential of the catalyst, modifying the molecular structure in combination with the metal identity and local environment (electrolyte composition, solvent, etc.) may afford a potent catalyst by modulating the binding of key intermediates. Examples supporting this proposed idea will be presented in the next section. However, before utilizing the electric field and introducing electrostatic interactions between the electrode and the attached molecule under current, it is vital to understand and possibly calculate the influence of the interfacial electric field around a molecularly modified electrode under similar circumstances.

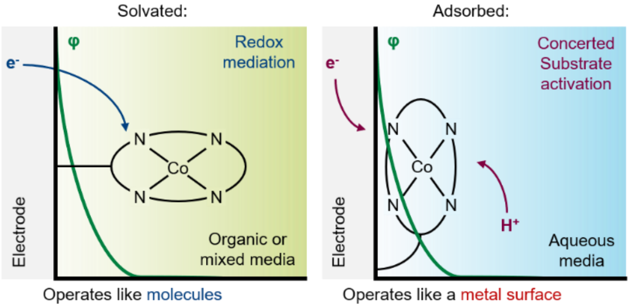

FIGURE 25. Strong electrostatic interactions between the electrode and immobilized cobalt complex caused by solvent-altered adsorption force the system to undergo two different mechanisms.[72] Reproduced with permission from Ref. 72. Copyright 2022 Nature Publishing Group.

4.2.1 Evaluating the strength of electric field on a modified electrode surface in CO_2 reduction

An exciting example published in 2018 by Clark *et al.* utilized a functionalized gold electrode via thiol linkage with a rhenium complex to investigate the interfacial electric fields in CO_2 reduction (**Figure 26**).[75] Investigations on the binding site of the catalyst provide insight into the strength and implications of the interfacial electric field. Sum frequency generation spectroscopy (SFG) and IR spectroscopy were employed to monitor the shifts of the carbonyl stretching modes in the adsorbed CO_2 on the immobilized electrode. CO stretching frequencies and amplitude strongly depended on the applied potential. The magnitude of the interfacial electric field was calculated to be 10^8–10^9 V/m based on experimental data. It is essential to see the direct relationship between the applied voltage, which can be manually controlled, and the strength of the interfacial electric field, which is considered to influence catalysis by influencing the binding mode of CO_2. Remarkably, the order of magnitude of the electric field strength determined in this work resembles the results determined inside active sites in a biological system that bridges the gap between enzymatic, homogenous, and heterogeneous catalysis.[116, 117]

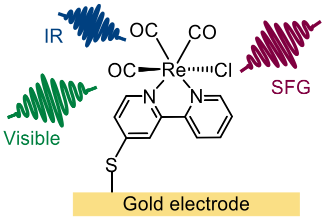

FIGURE 26. Study the electric field on the electrode surface modified with a Re complex (SFG, sum frequency generation spectroscopy).[75] Reproduced with permission from Ref. 75. Copyright 2018 American Chemical Society.

4.2.2 Electrostatic interaction induced by charged functional groups

In addition to externally applied electric fields, local electric fields introduced by charged functional groups could also be employed to tune catalytic activity, for example, in organometallic catalysts.[118-124] In molecular catalysis involving organometallic complexes, the supporting ligand plays a crucial role in controlling the reactivity and selectivity of the catalytically active species by tuning its electronic and steric properties.[125] Recent studies on the effects of ligand substituents on molecular electrocatalysis emphasize the importance of considering possible through-space effects caused by the installed substituents in addition to the inductive effects (through-structure) that are commonly interpreted on the molecular level.[126, 127] In other words, the implementation of charged substituents on the molecular functionality being immobilized, for example, not only alters the electronic properties of that molecular functionality by donating or withdrawing electrons but also may induce electrostatic effects which may play an irreplaceable role in stabilizing key intermediates in small molecule transformations.

The major challenge remains on disentangle the inductive (through-structure) and electrostatic (through-space) effects.[125, 126, 128-130] A series of homogenous substituted iron porphyrins have been systematically studied by Savéant and coworkers for CO_2 reduction. Installing an electron-withdrawing substituent was found to lower the overpotential by reducing the electron density around the metal center. In contrast, electron-donating substituents were observed to behave the opposite.[126, 128, 131] A linear correlation between log(turnover frequency) and the standard potential was found when the electronic inductive effect of the substituents was taken into account. However, importantly, incorporating charged substituents stabilized key intermediates through electrostatic attraction or repulsion, causing a significant deviation of those catalysts from the linear correlation.[126] Additionally, effects of sterically hindered substituents on the aggregation of catalysts in the immobilized system have to be taken into account.[132, 133] **Figure 27** depicts the homogeneous iron porphyrin complexes mentioned in the previous discussion. The presence of electron-donating and electron-withdrawing substituents resulted in well-understood inductive effect whereas the presence of positively and negatively charged substituents on the ligand resulted in through-space electrostatic effects which is rather challenging to disentangle from the inductive effect.[128, 129, 132] Being able to form hydrogen bonding between the ligand and substrate could also help with stabilizing intermediate. Based on the understanding of the homogenous system, Gotz *et al.*, presented a study on the influences of mesityl and thiophene peripheral substituents asserted on surface attachment.[132] Iron porphyrin complexes with thiophenyl substituents created a dense and planar molecular layer on the silver electrode, embedded with facile electron transfer via Ag-S covalent bonds. On the contrary, bulky mesityl substituents caused less dense coverage of the molecular layer and created less stable interactions. It is important to note that the bulky mesityl groups, which were proved to prevent catalyst aggregation and improve catalytic behavior in solution, now exert a negative effect after immobilization. We note that molecular electrostatic effects significantly affect the catalytic activity and selectivity. Meanwhile, implications of the substituents on the ligands for hybridized metal complexes should also be deliberated after immobilization.

Interestingly enough, introducing sterically hindered substituents on the ligand was found to suppress catalyst aggregation and increase catalytic activity in the case of immobilized cobalt complex, despite the decrease in the coverage of catalyst. Prolonged catalytic lifetime was observed in the immobilized cobalt octaalkoxyphthalocyanine (CoPc) catayzed CO_2 reduction. CoPc was anchored on a graphene sheet via π-π stacking, showing that the alkoxy substitution on the ligand improved the catalytic activity to over 30 hours (**Figure 28**).[133] The opposite impacts of sterically hindered substituents on the metal complex observed in the two hybrid systems: iron complex modified silver electrode catalyzed oxygen reduction reactions and cobalt complex modified electrode catalyzed CO_2 reduction pose the challenges remain on predicting the role of the substituents for optimal design.

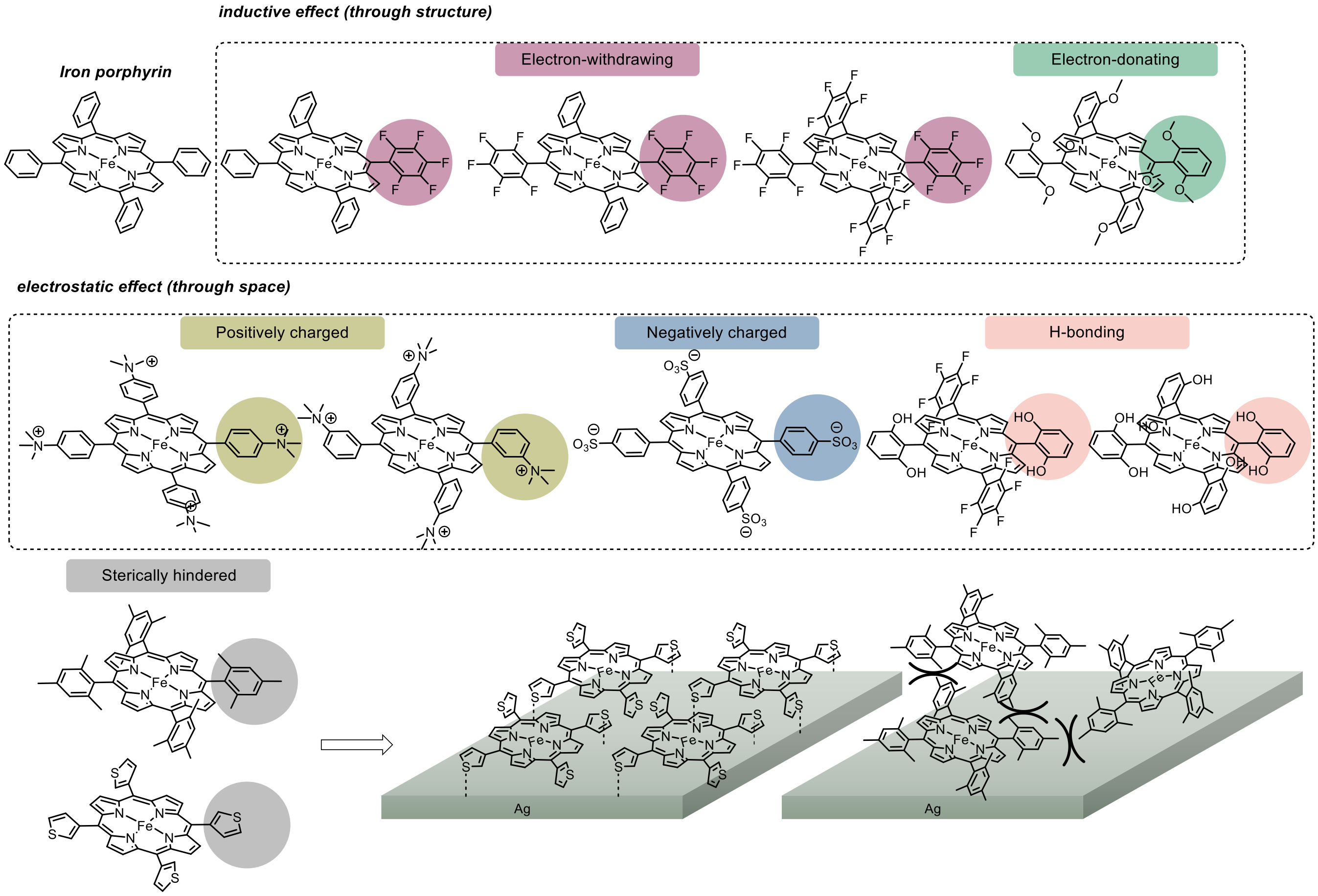

FIGURE 27. Representations of iron porphyrin complexes with electron-withdrawing, electron-donating, positively, and negatively charged substituents on porphyrin, as well as substituents that possibly introduce H-bonding formation. Homogenous iron complex with thiophenyl created a relatively dense molecular layer on electrode surface, whereas bulky mesityl substituents resulted in less stable interaction with the electrode surface and created less dense surface coverage.

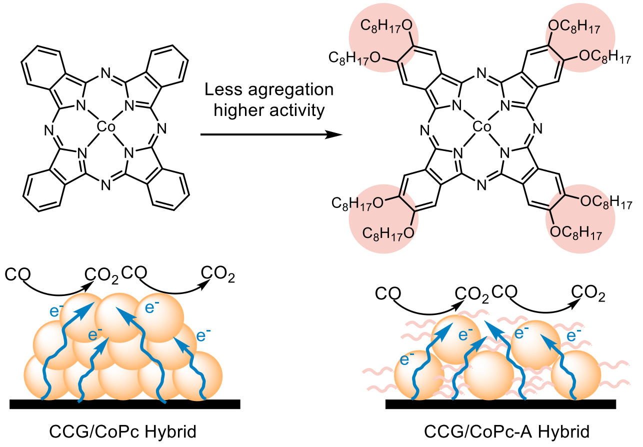

FIGURE 28. Ligand substitution of immobilized cobalt complex reduces aggregation; CCG stands for chemically converted graphene.[133] Reproduced with permission from Ref. 133. Copyright 2019 American Chemical Society.

To disentangle the through-bond inductive and through-space effects, Savéant and coworkers took advantage of computational methods for separate evaluations.[127] Realizing the importance of electrostatic stabilization in heterogeneous catalysis,[134, 135] especially for energy related transformations such as CO_2 reduction,[114, 115, 126, 136] is beneficial to the logic design of the heterogenized catalyst. Cobalt porphyrin was chosen again and immobilized on carbon paper. Selective production of CO from CO_2 reduction was achieved with a Faradaic efficiency of 95%. Investigation of peripheral functionalities on the porphyrin ligand indicated an increase in electron density of the cobalt center by introducing electron-donating substituents on the ligand that, in turn, increased CO_2 adsorption, thus facilitating the reaction (**Figure 29**). Quantification of electronegativity using density functional theory (DFT) via Mulliken population analysis on hydrogen charge densities was conducted. Along with experimental results, further proved the association between the inductive effect of the substituents and the electronic structure at the cobalt center. Cationic functionalities, on the other hand, were found to form a favored electrostatic stabilization with the key intermediate in the rate-limiting step and also increase the activity. The opposite catalytic behavior was observed when anionic functionalities were investigated, supporting the electrostatic hypothesis. Once again, considering electrostatic effects in addition to inductive electronic effects for ligand substitutions is essential for a rational design of a molecularly modified electrochemical system.

Ligand substitution could exert extra through-space stabilization to key intermediates and provide coordination sites to the electrode to create strong interaction depending on the immobilization method. Meanwhile, substituents exert inductive effect to the electronic structure of the catalytically active metal center. Furthermore, bulky substituents may decrease the possibility of aggregation but the density of the catalyst coverage at the same time. It is worth noting that the optimal ligand design for the organometallic catalyst may not perform the best in the immobilized form, as demonstrated in the iron porphyrin complex bearing mesityl substituents.[132] The underlined importance and complexity of ligand substitution effects should be considered when designing an immobilized molecular catalyst for optimal performance.

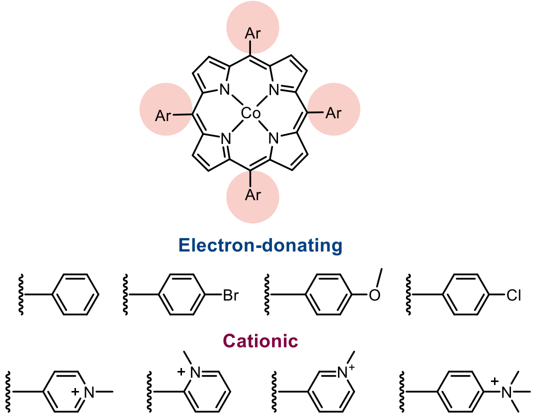

FIGURE 29. Investigation on ligand substitution effect on immobilized Co catalyzed CO_2 reduction.[127] Reproduced with permission from Ref. 127. Copyright 2019 The Royal Society of Chemistry.

4.3 Exploring small molecule transformations beyond energy conversion: switchable catalysis

The molecularly modified electrode provides ready access to electrons and an electric field. Accurate control over the potential being applied to the electric cell allows precise tuning of the immobilized functionalities on the electrode, emerging as a powerful tool for achieving temporal control in switchable catalysis.[49, 137-139] The electronic properties of a molecular component that can be tuned traditionally by implementing electron-donating/withdrawing substituents now could be replaced by an incrementally applied potential.[70] *In situ* alternation of the electronic property (electron sufficient/deficient) on a substrate during a reaction process that could not be accomplished by molecular modification could be circumvented in a hybrid system. Different redox states of a catalytically active metal center in anchored organometallic catalysts can be modulated on demand by applying different potentials.

4.3.1 Modulating electronic properties of the molecular attachment through the voltage applied

Immobilization of molecules onto electrodes has been focused on anchoring molecules that participate in redox reactions as discussed above.[30, 33, 140] Heterogenization of a molecular catalyst onto an electric-addressable surface helps reduce the kinetic barrier of electron transfer within the double layer. However, as mentioned in the above examples, the molecularly modified electrode is not limited to serving as the catalytically active species. In **Section 4.2**, we discussed the interfacial electrostatic interaction induced by an electric field and inductive and through-space effects caused by ligand substitution. However, the electronic properties of an attached molecule could be tuned, in principle, by the applied electric field instead of chemical modifications of the molecular structure. A recent study on electron-inductive effects took advantage of molecularly modified electrodes as functional groups in cross-coupling and amidation reactions to replace traditional electron-donating and withdrawing substituents on the substrates.[77] The electronic properties of the molecules being immobilized on the gold electrode could be tuned by applying different voltages: applying a negative potential imitated electron-donating groups, whereas a positive potential imitated electron-withdrawing groups. By doing so, a continuous and *in situ* tuning of the electronic property was performed on the substrate (**Figure 30**). For example, in a Pd-catalyzed Suzuki-Miyaura cross-coupling reaction, the reaction rate was slowest at +0.3 V and increased upon applying a negative potential. The highest activity was reached at -0.15 V, as monitored by SERS (**Figure 30a**). This observation agreed with the trend observed when an electron-donating substitution was performed on the arylbromide substrate. Alternating the electronic property of the substrate throughout the catalytic cycle could be very challenging but may enhance the activity dramatically for the steps that require opposite electron-inductive effects. For example, the amidation reaction (**Figure 30b**) could be accelerated when 1) the nucleophilicity of the oxygen in the carboxylic acid was enhanced and 2) the electrophilicity of the carbonyl carbon in O-acylurea was enhanced. Applying a negative voltage first, then inverting to a positive voltage should facilitate the reaction. Applying -0.7 V and then switching to +0.4 V did increase the intensity of the peak of the desired product in SERS. This study showcases the possibility of utilizing electrodes as functional groups of the immobilized molecules by switching the voltage between positive and negative values to mimic electron-withdrawing and donating effects. The electron-inductive effect could be well extended to the immobilized catalyst in different catalytic systems to satisfy various electronic demands on the catalyst. This study also opens up the field of electrosynthesis in redox and non-redox reactions: in addition to directly supplying and withdrawing electrons, the electrostatic effect provided by the electrode could also be considered or employed as a tool.

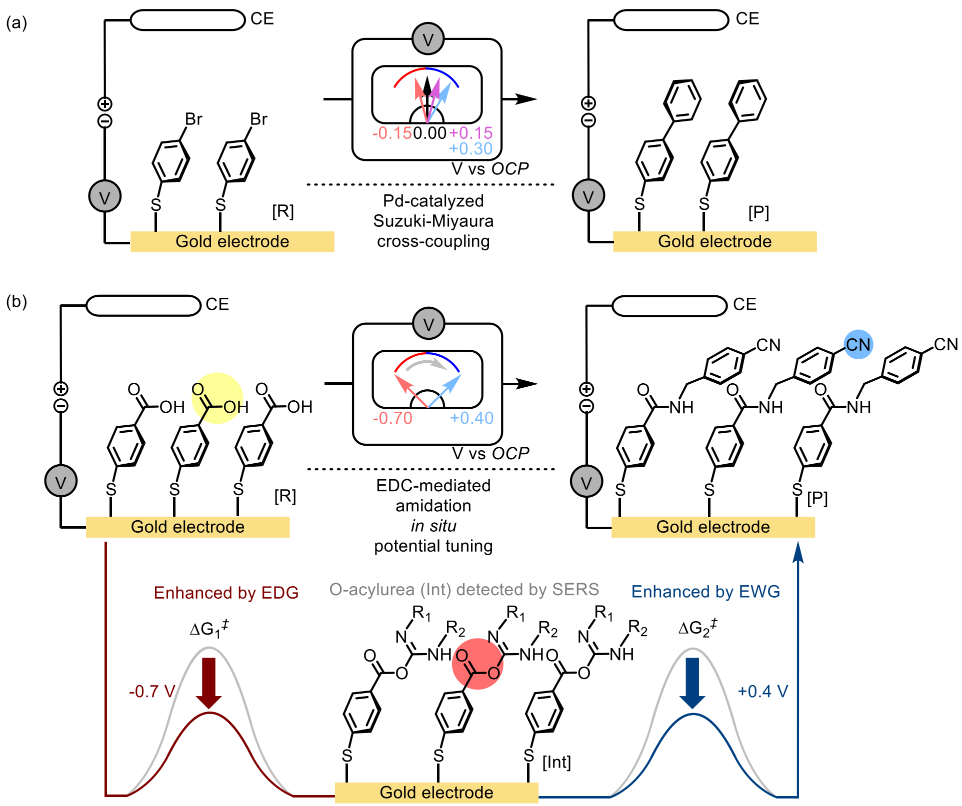

FIGURE 30. (a) Palladium-catalyzed Suzuki-Miyaura cross-coupling reaction, and (b) carbodiimide-mediated amidation reaction (CE, counter electrode; EDG, electro-donating group; EWG, electron-withdrawing group; OCP, open circuit potential; [R], reactant; [P], product; Int, intermediate; $\Delta G^{\ddagger}$, Gibbs free-energy barrier).[77] Reprinted with permission from AAAS.

4.3.2 Redox-switchable polymerization mediated by iron complex immobilized on an electrode surface

Another interesting field of utilizing molecularly functionalized electrode surface focuses on introducing spatial and temporal control in polymerization reactions. Switchable catalysis can be achieved by electrochemically altering the oxidation state of a catalytically active metal center. Electrochemically control of molecular catalysts in switchable polymerization has been reported for atomic transfer radical polymerization (ATRP),[141] cationic polymerizations,[142] and ring-opening polymerizations.[137, 143-145] The selective application of an electrical stimulus to trigger redox events on a redox-active metal complex provides an alternative way to chemically controlled redox events. In particular, electrochemical control in redox-switchable polymerization reactions alleviates the need for additional chemicals in these processes. It further enables multiple switches when possible. Switching between reductive and oxidative potentials allows on/off control of the polymerization process, control over molecular weights and dispersity, as well as over the stereochemistry and composition of the polymer chain.[49, 137, 141-146]. Enabling surface-initiated polymerization by immobilizing redox-active metal complexes onto an electrically addressable surface with the selective application of an electrical stimulus would allow electrochemical control to afford valuable polymeric materials. One could expect that the combination of electrochemistry associated with the solid support and molecular properties of the metal complex should evolve the field of switchable polymerization.

However, reports on combining the advantages of surface-initiate polymerization with electrochemically controlled polymerization are rare. Byers, Wang, and coworkers presented impressive work on electrochemically controlled surface-initiated polymerization catalyzed by iron complexes anchored on an electrode surface (**Figure 31**).[49] A bis(imino)pyridine iron(II) complex was anchored onto titanium oxide nanoparticles through protonolysis of an iron alkyl precursor surface with alcohol groups. The surface-supported redox-active iron complex was achieved by depositing the functionalized titanium oxide nanoparticles onto a fluorine-doped tin oxide surface, serving as the electrically addressable surface for electrochemical polymerization. The reactivity of the molecular iron complex toward ring opening polymerization of lactide (LA) and cyclohexene oxide (CHO) was maintained after surface functionalization. Both homogenous and heterogenized iron(II) complexes react with lactide in the reduced state. Oxidizing the iron(II) center to iron(III) by using a chemical oxidant resulted in no activity toward lactide but initiated the polymerization of CHO. Applying an oxidative potential to replace chemical oxidants resulted in the same switchable behavior for both homogenous and surface-anchored iron complexes.

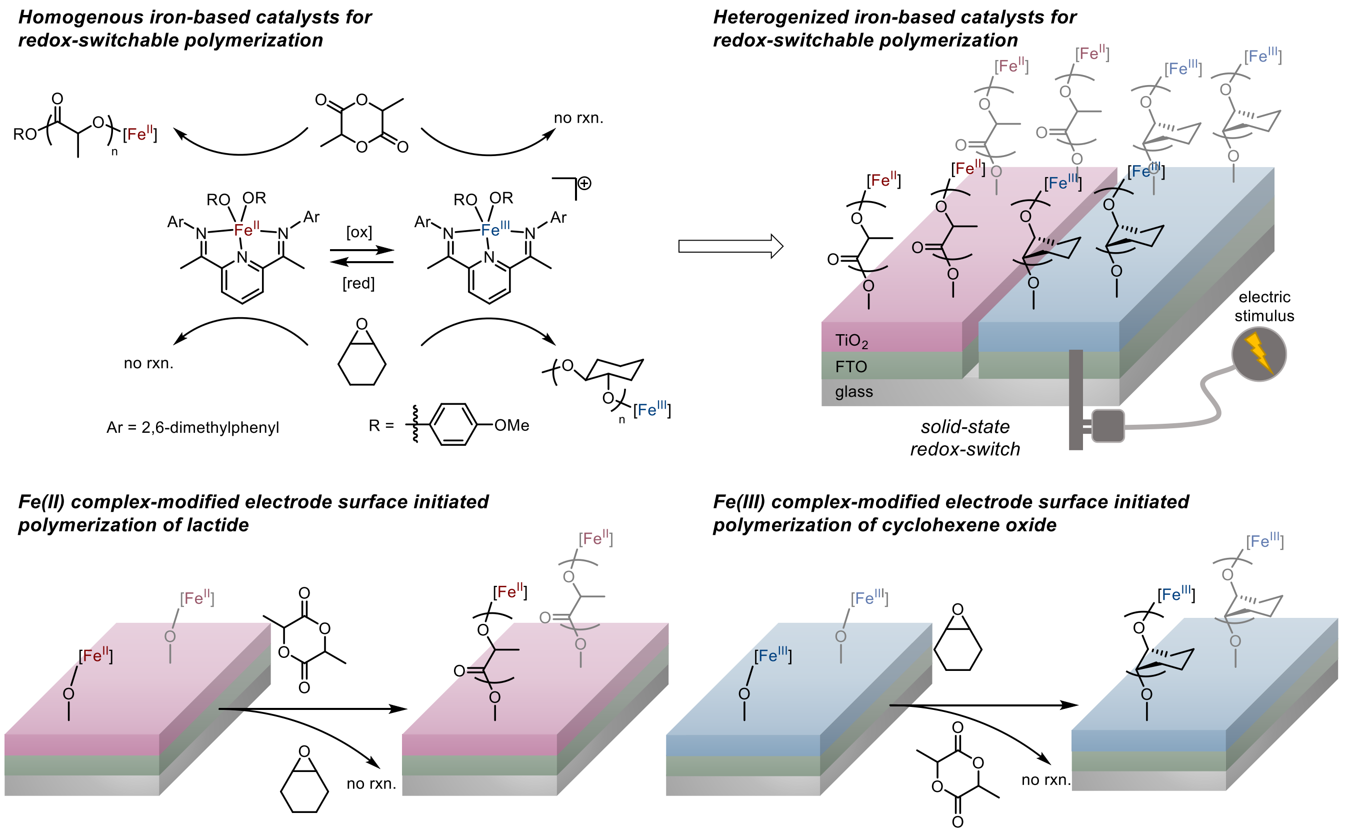

FIGURE 31. Iron-based catalysts for redox-switchable polymerization of lactide and epoxides are heterogenized onto the electrode surface. The reactivity of the appended iron-based catalyst was altered by an electrochemical switch.[49] Reproduced with permission from Ref. 49. Copyright 2021 The Royal Society of Chemistry.

Importantly, a cyclic voltammetry study on the electrochemical property of the heterogenized iron complex suggested redox events associated with surface-bound species similar to the homogeneous case. Additionally, the polymer chains remained attached to the surface without cleavage. Inspired by the selective behavior of electrochemically controlled iron(II)/(III) catalyzed polymerization, a substrate containing two electrically isolated domains was used to demonstrate the spatial control of polymer composition by exposing one domain to an oxidizing potential, which resulted in patterns of polylactide (PLA) and polycyclohexene oxide (PCHO) through the sequential addition of the two corresponding monomers. It is noteworthy that exposing a combination of iron(II) and iron(III) functionalized electrodes in the mixture of lactide and cyclohexene oxide resulted in the chemoselective growth of PLA and PCHO on the iron(II) and iron(III) electrode, respectively, while exposing two electrically isolated domains to a mixture of monomers also resulted in selective polymerization. This study demonstrates a successful case of electrochemically controlled polymerization via a molecular functionalized electrode surface in which an electrical potential altered the redox state of the immobilized catalyst, therefore affecting the catalyst's reactivity and enabling a selective polymerization of two monomers. As a result, a spatially controlled surface polymerization pattern was achieved by switching the oxidation state of the iron complexes on two isolated domains in one system. One of the limitations of immobilizing metal complexes through directly ligating the active metal center to the surface is that as the polymerization proceeds, the metal moves further away from the surface, which may result in an inefficient electron transfer from the electrode surface to the catalyst. Secondly, the redox property of the complex directly connected to the surface via a hydroxyl linkage differs from the polymer-bound metal complex after the polymer chain is formed. Nonetheless, this study demonstrated proof-of-concept case for achieving an on/off switch in polymerizing different monomers by electrochemically triggered redox events.

5. SUMMARY AND OUTLOOK

Throughout this review, we tried to convey the potential advantages of employing a molecularly modified electrode/electrically addressable material as a catalyst for electrocatalytic reactions related to energy conversion and transformations strongly impacted by an electric field. We started by demonstrating common methods for the surface immobilization of molecules, mainly non-covalent and covalent interactions. We included several commonly employed electrically addressable materials, such as carbon-based, metal, and oxide-based electrodes. Common strategies being applied to modify each type of electrode material were discussed, along with techniques for characterizing the resulting material. To provide a handle for immobilization, certain modifications are required to be implemented on the molecular component. The resulting “linkage” to the surface often plays an important role in manipulating electron transfer and determining the reaction mechanism. With an overview of some recent publications working on redox and non-redox reactions utilizing molecularly modified electrodes as a catalyst, we discussed the importance of the molecular component of the hybrid system that provides handles to optimize the reactivity and selectivity of the reaction studied by modifying the molecular structure. Such modifications on the molecular level could result in inductive electronic effects, steric effects, as well as electrostatic effects. We hope to encourage further designs and investigations on combining the advantages of homogenous molecular catalysts and heterogeneous electrode materials for optimal activity, selectivity, durability, and efficiency of a catalytic system. To provide an excellent reference point for beginners in the field, we summarize the following learning points from this review and wish to inspire more people to explore this area.

1) Select the molecular component and the electrode material to start

A homogenous metal complex with optimal catalytic behavior is often a good starting point for a well-known reaction. Similarly, there is sometimes a good combination of electrode materials. However, there are several things to keep in mind: (i) Implementing the molecular handle for immobilization may affect the catalytic behavior of the catalyst; (ii) Successful immobilization does not mean an invariable translation of the reactivity of the homogenous catalyst to the hybrid system.

2) Implement handles for immobilization by surface functionalization and molecular modifications

Learning from the examples discussed in Section 2, one should have an idea how to immobilize a specific type of molecular catalyst onto an electrode surface. Depending on the reaction, the mechanism involved, the tunability of both components, a particular immobilization method is more advantageous than another. Meanwhile, the type of interaction created between the molecular species and the electrode, for example, covalent linkage, differences in linkage type (degree of conjugation), linkage length, and linkage flexibility must be considered. Additionally, as observed in many cases, more than one type of interaction may be present in the resulting system.

3) Utilize different characterization methods to understand the hybrid system

As mentioned above, cyclic voltammetry is a convenient tool to characterize redox-active surface-anchored molecular catalysts. However, strong electrostatic interaction between the metal center and the electrode will limit the utility of cyclic voltammetry. Instead, cyclic voltammetry could produce confusing results, such as the lack of clear redox peaks. To address this issue, other characterization tools should be employed to assist surface analysis for the hybrid system, such as X-ray techniques that can help examine the existence of metal centers, their oxidation state, and their coordination environment.

4) Consider possible implications of immobilization

It is common to observe more than one type of interaction in a hybrid system between the electrode material and the anchored metal complex, with implications in understanding the system. Besides linkages created on purpose, axial coordination from a metal center to the electrode, depending on the available orientation of the immobilized compound, could be expected. In addition, possible inductive effects from electron-donating/withdrawing substitutions, through-space effects resulting from charged substitutions, and steric hindrance introduced by bulky substitutions on the molecular structure need to be considered. Since electrochemistry is evaluated in an electric cell, an electric field may impact the catalytic performance. Electrolytes and solvents also play a crucial role in altering catalytic behavior and are worth evaluating when engineering a hybrid system.

5) Expand the reaction scope of the intended study

A significant effort of the molecularly modified electrochemical system focuses on energy-related reactions, with only a few studies demonstrating applications in small molecule synthesis. However, with the last section, we hope to initiate innovative thinking on possibly adopting hybrid catalyst systems for other reactions.

Although many reports on immobilization methods and studies investigating catalytic activity with hybrid systems for electrical and chemical transformations have been presented, problems still remain. The catalytic behavior of the molecular catalyst does not transcribe unchangeably to the immobilized state. Discussions on the effects of linkages of different types and lengths involved in heterogenization and what linkage/immobilization to choose are still ongoing. In some cases, the linkage is not expected to be as contributory and influential as in other circumstances when all other system components are evaluated. In another scenario, for example, the strong conjugation between the electrode and the catalyst is key to the system's uniqueness. Implementing functional groups on a ligand either exerts a positive or negative impact on the reactivity, and requires a comprehensive understanding of the inductive and electrostatic effects for structure optimization. Fundamental studies of the electrode/electrolyte interface, electron transfer kinetics, and electron-proton coupled/decoupled pathways need to be conducted.[78] Although less elaborated in this review, we would like to emphasize the importance of the bulk environment in which reactions occur. Solvent and electrolyte, for example, could decide on the reaction pathway and certainly need to be included in the design.

The applications of electrochemistry in chemical synthesis, although not discussed in detail in this review, have been established in homogenous catalysis.[3, 147-149] Furthermore, the coupling of multiple catalysts after a well-established electrochemical transformation, such as CO_2 reduction, allows subsequent reactions to produce valuable products such as ethylene.[78, 150, 151] Applying a compatible catalyst that allows orthogonal chemistry to occur has excellent potential in synthesizing complicated chemicals from simple building blocks. One of the challenges remains in the design of a practical, large-scale electrochemical setups. Although electrochemical cells offer proof-of-concept for some reactions, they may not be suitable for industrial applications. Notably, an electrochemical cell can switch catalysis on and off rapidly; scaling up may encounter the limitation of mass transport within the cell. A designed flow cell has been developed and adopted to address the potential issue in large-scale electrochemical synthesis.[9] Other than the scale-up issue, another potential disadvantage of the switchable electrochemical synthesis is a low-value charge balance reaction from sacrificial counter electrodes, i.e., lithium,[139] magnesium.[137] A way to solve the issue is to employ an integrated catalysis strategy.[152] For example, a value-added process (i.e., CO_2 to syngas) in the counter chamber can be coupled with a targeted reaction to reduce the energy loss during electrolysis (**Figure 32**).[48]

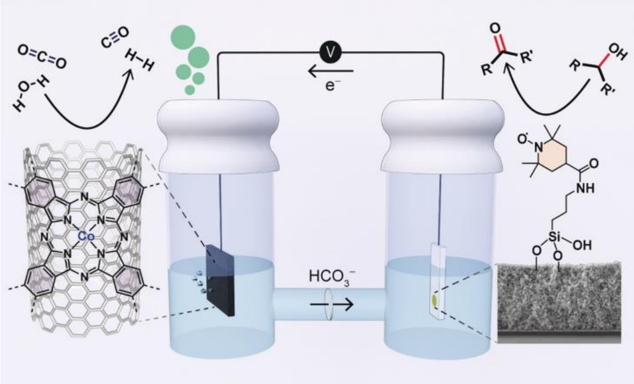

FIGURE 32. Integration of alcohol oxidation and CO_2-to-syngas conversion in the same electrochemical setup.[48] Reproduced with permission from Ref. 48. Copyright 2020 John Wiley & Sons, Inc.

In summary, we highlight the potential of immobilizing molecular catalysts, especially organometallic catalysts, onto electrodes to afford a potent catalytic material to interconvert electrical and chemical energy. Such a hybrid system is constructed from a modified electrically addressable surface and metal complexes via a handful of immobilization methods. Effects on electron transfer rate, activity enhancement, product selectivity, and catalyst lifetime are discussed. Implications of functional groups, external electric field, and solvent are emphasized for catalyst optimization. The easy, ready, and precise access to electric current provides an excellent avenue toward temporal control and redox altering of a catalyst's behavior. Implementing orthogonal chemistry with electrochemical transformations represents a future direction of accomplishing complicated syntheses from simple building blocks such as CO_2. Overall, the surface functionalization of molecular compounds on an electrically addressable surface heralds a new paradigm in designing and conducting chemical transformations.

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Author Contributions

The manuscript was written through contributions of all authors. All authors assisted during the manuscript preparation. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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