

Modified Working Electrodes for Organic Electrosynthesis

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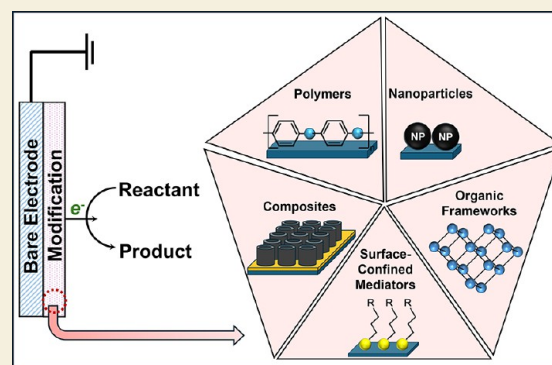
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ABSTRACT: Organic electrosynthesis has gained much attention over the last few decades as a promising alternative to traditional synthesis methods. Electrochemical approaches offer numerous advantages over traditional organic synthesis procedures. One of the most interesting aspects of electroorganic synthesis is the ability to tune many parameters to affect the outcome of the reaction of interest. One such parameter is the composition of the working electrode. By changing the electrode material, one can influence the selectivity, product distribution, and rate of organic reactions. In this Review, we describe several electrode materials and modifications with applications in organic electrosynthetic transformations. Included in this discussion are modifications of electrodes with nanoparticles, composite materials, polymers, organic frameworks, and surface-bound mediators. We first discuss the important physicochemical and electrochemical properties of each material. Then, we briefly summarize several relevant examples of each class of electrodes, with the goal of providing readers with a catalog of electrode materials for a wide variety of organic syntheses.

KEYWORDS: Heterogeneous Electrocatalysis, Organic Electrosynthesis, Working Electrode, Organic Framework, Metal Nanoparticles, Surface-Grafted Mediators, Self-Assembled Monolayer, Composite Semiconductors, Conductive Polymer, Redox Polymer



1. INTRODUCTION

The very first report of an electrosynthetic reaction dates back to the mid-19th century.^{1–3} Since then, the field of electrosynthesis has undergone significant development. Compared to traditional synthetic processes, electrosynthesis is more environmentally friendly and less expensive as it replaces reagents, catalysts, and the input of excess heat with electricity. Moreover, electrosynthetic processes can be scaled up to address industrial demand.^{4–8} For example, a variety of compounds, such as chlorine gas, aluminum, copper, and nylon, are produced in metric tons using electrochemical methods.^{9,10}

As mentioned previously, a majority of large-scale electrosynthesis examples involve simple inorganic products. However, within the last two decades, significant attention has been dedicated to developing electrochemical methods to form small organic molecules with various applications, such as in pharmaceuticals and agriculture.^{7,11–13} Two major challenges in developing new electroorganic reaction schemes are (i) optimizing reaction conditions to achieve the highest yield while requiring the lowest amount of auxiliary reagents and energy input and (ii) developing a suite of analytical methodologies to study complicated reaction mechanisms at the molecular scale with precision.^{14,15}

For the most ideal reaction conditions, research efforts mainly focus on parameters in the solution phase, such as temperature, solvent/supporting electrolyte composition, and molecular electrocatalysts, to increase the yield of the reaction and induce desired regio- and stereoselectivity.^{11,13} As such, homogeneous electrocatalysis has been heavily studied in organic electrochemistry as it enhances the rate of the reaction and decreases the applied electrochemical potential needed to drive the reaction of interest, thereby reducing costs and increasing the efficiency of the desired reaction.^{16–19}

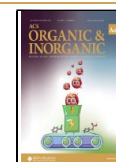
One of the less-explored areas of research in organic electrochemistry, however, is the role of the working electrode (WE) and engineering of the interface of the WE and the solvent system. In this context, it is important to recognize that electrochemistry is an interfacial science, where the most crucial

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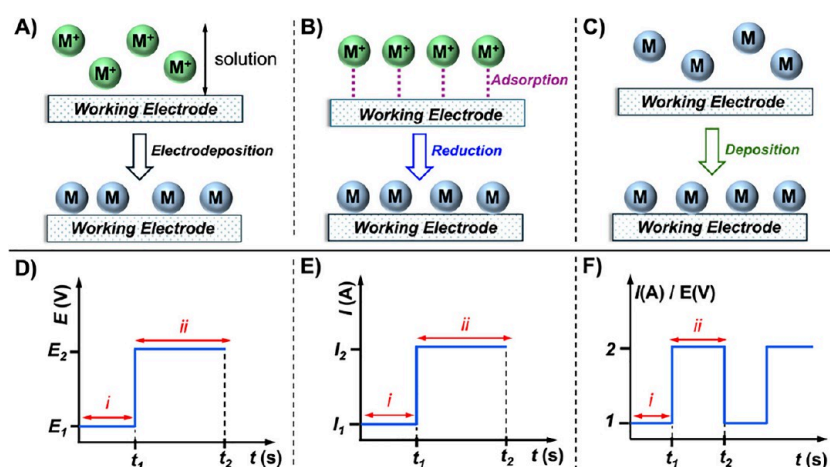


Figure 1. Various strategies for decoration of a WE with NPs including (A) electrodeposition from a metal-cation dissolved in solution, (B) attachment of a metal-cation to the WE and subsequent reduction, and (C) direct deposition of NPs to the WE using physisorption. Three major electrodeposition methods are (D) potentiostatic, (E) galvanostatic, and (F) pulse. In panels D–F, *i* and *ii* represent absence and occurrence of the electrodeposition events.

part of the process (i.e., heterogeneous electron transfer) occurs at the interface of the WE and solvent system. Beyond being the sink or source of electrons, the WE can also serve as an electrocatalyst, which is referred to as heterogeneous electrocatalysis.^{20–23} Compared to the homogeneous approach, heterogeneous electrocatalysis is more appealing for large-scale electroorganic reactions as it decreases separation costs, and the electrocatalyst can be reused for several reaction cycles. Moreover, the reusability of heterogeneous electrocatalysts can be easily evaluated using various electrochemical methods and surface analysis methodologies such as X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).^{24,25}

Given the rapid growth in the fields of organic electrochemistry and materials science and the crucial role of the WE in electroorganic reactions, it is imperative to briefly review the latest efforts in utilizing novel approaches to (i) modify electrochemical properties of simple metallic or carbonaceous WEs and (ii) engineer the interface of the WE and solvent. Herein, we shed light on various strategies to modify metallic and carbonaceous WEs and use of modified WEs for electroorganic reactions. The modification approaches covered in this Review include nanoparticles, composite semiconductors, redox-active and conductive polymers, organic frameworks, and self-assembled and surface-grafted molecular electrocatalysts. It is worth noting that this Review excludes metallic and carbonaceous WEs as well as bioelectrocatalysts and bioelectrodes. Readers interested in these topics and the use of such electrodes in organic electrochemistry are encouraged to consult other existing literature.^{26–33}

2. ELECTRODE MODIFICATION WITH NANOPARTICLES

2.1. Nanoparticles as Electrocatalysts

Generally, particles with sizes ranging from 1 to 100 nm are referred to as nanoparticles (NPs).³⁴ Compared to the bulk material, NPs can have distinctly different optical, magnetic, and chemical properties.³⁵ NPs have been classified based on various properties such as particle shape, composition, and size distribution.^{36–38} Among various types of NPs, metal and metal oxide NPs found significant attention as efficient catalysts

for various chemical processes.^{39–42} This growth in popularity is rooted in lower chemical toxicity of NPs compared to their homogeneous catalyst counterpart. Moreover, NPs immobilized on a substrate can be easily removed from the reaction mixture, thus minimizing the problem of an additional separation step and loss of catalyst that has plagued the use of homogeneous catalysts in large-scale chemical processes.^{43,44}

In electrochemical studies, macroscale electrodes were modified with NPs to take advantage of their unique properties.^{45,46} As such, metallic and metal oxide NPs are heavily studied as promising electrocatalysts for efficient reduction of small molecules and ions such as H⁺,⁴⁷ CO₂,^{48,49} and H₂O,^{50,51} as well as oxidation of small-chain aliphatic alcohols (e.g., methanol and ethanol) in fuel cells.⁵² Electrode modification with NPs features myriads of advantages such as high surface area, improved electrocatalytic properties, enhanced control over microenvironments, and low cost for electrode preparation.^{53,54} Increasing surface area together with inducing novel electrocatalytic properties culminates in higher current densities at low NP loading amounts, making this type of electrode modification extremely desirable for practical applications.⁵⁴

One emerging avenue of research is to leverage electrocatalytic properties of metallic and metal oxide NPs for electroorganic transformations such as carboxylation reactions and various types of cross-coupling processes. In the following section, we first examine practical considerations for electrode modifications with NPs. Next, we shed light on several important examples where electrodes decorated with NPs were employed in electroorganic reactions.

2.2. Methods for NP Synthesis and Electrode Modification

There are a wide variety of methods to modify surfaces with NPs. For electrochemical applications, however, methods for preparing NP-modified electrodes can broadly be classified into one of three categories depending on the order of formation and immobilization (Figure 1).⁵⁵ The first category involves single-step processes wherein formation and immobilization of NPs occur simultaneously (Figure 1A).⁵⁵ The second category involves two-step processes wherein metal ions are immobilized on the support electrode and subsequently reduced, either chemically or electrochemically, to form NPs directly on the

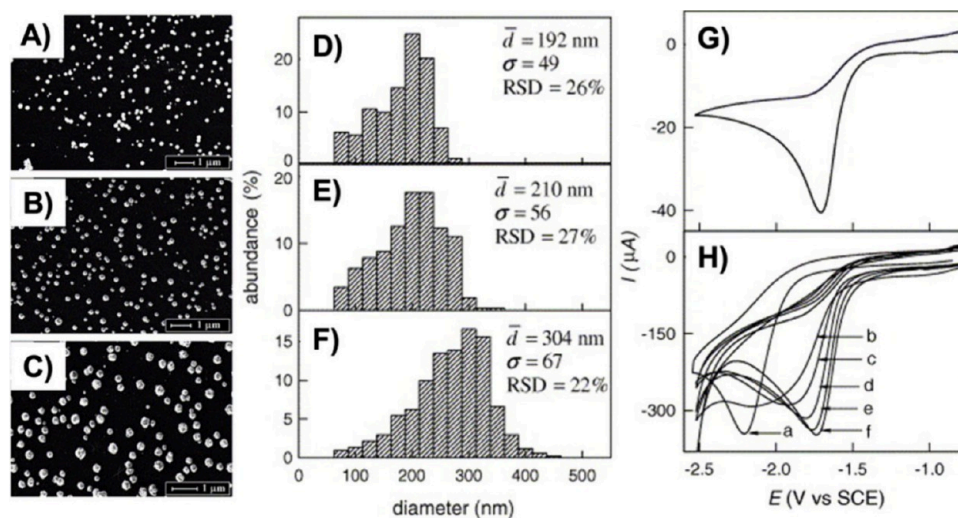


Figure 2. Impact of electrodeposition time on particle size and distribution with pulse durations of (A, D) 30 s, (B, E) 50 s, and (C, F) 90 s. Panels A–C show scanning electron microscopy (SEM) analysis. Panels D–F represent corresponding particle counts. Electrodeposition was carried out on GC by potential steps from 0.5 to -0.4 V vs Ag/Ag⁺. CV studies with (G) GC and (H) GC modified with Ag NPs electrodeposited for (b) 20, (c) 30, (d) 50, (e) 70, and (f) 90 s. Reprinted from ref 75. Copyright 2006 with permission from Elsevier.

electrode surface (Figure 1B).⁵⁵ The primary challenge with this approach is the introduction of functional groups that coordinate with the metal precursor on the electrode surface.⁵⁵ This challenge can be overcome by encapsulating metal ions in a polyelectrolyte film on the electrode surface or by modifying the electrode surface by diazonium coupling.^{56,57} The details of such procedures are mentioned elsewhere.^{56,57} The third category involves two-step processes in which NPs are first synthesized in solution before being immobilized on the support electrode (Figure 1C). Compared to the previous two categories, methods belonging to this category offer optimal control over NP size and shape by separating NP formation and immobilization. NPs are most often prepared in solution by colloidal synthesis. As for the deposition method, various strategies such as drop-casting and spin-coating decoration have been widely employed.^{55,58–60}

Electrodeposition is one of the most popular methods to decorate WEs with NPs. With electrodeposition, NPs are directly deposited onto the surface of the WE from a solution containing the metal ion upon the application of electrical current or electrochemical potential.⁶¹ Electrodeposition is an excellent method compared to other approaches for modification of WEs with NPs due to its simplicity and offering large control over particle shape, size, and distribution by tuning experimental parameters such as deposition potential or current, time, temperature, and electrolyte composition.^{62–65} Potentiostatic, galvanostatic, and pulse are three major electrodeposition approaches.⁶⁶ In potentiostatic electrodeposition, the potential of the WE is held at a fixed electrochemical potential of E_2 , which is at least 200 mV more negative than the formal reduction of the metal-cation, for a set duration (Figure 1D). With the galvanostatic method, a set electrical current is applied to the WE for a prescribed duration to accomplish NP electrodeposition (Figure 1E). For both potentiostatic and galvanostatic electrodeposition, optimal WE modification is inextricably linked to several considerations such as magnitude of applied electrochemical potential or electrical current, duration of electrodeposition, and concentration of metal precursor.⁶⁷ Finally, with pulsed electrodeposition, a series of electrochemical potential or electrical current pulses with fixed frequency and magnitude is applied to the WE (Figure 1F).⁶⁶

Pulsed electrodeposition is more complex than both potentiostatic and galvanostatic methods in that the properties of applied pulses in addition to solution composition can effect the outcome of the electrodeposition.^{63,68}

Besides electrochemical considerations, it has also been found that the extent of WE modification with NPs is sensitive to the underlying electrode material. As such, porous substrates, such as reticulated vitreous carbon (RVC) and carbon felt, are excellent candidates as they provide greater surface area for electrodeposition and minimize particle dislocation and detachment.^{54,69}

2.3. NP-Modified Electrodes for Electroorganic Reactions

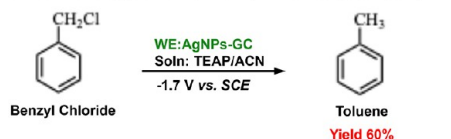
Silver (Ag) is a well-known cathode material as it shows an electrocatalytic response for the reductive cleavage of the C–X (X = Cl, Br, I) moiety. Use of the Ag cathode for various electroorganic reactions and relevant mechanistic studies has been extensively investigated by several pioneers in the field of organic electrochemistry such as Peters,⁷⁰ Gennaro,^{71,72} and Amatore.^{73,74} Compared with a bare Ag cathode, modifying a carbonaceous WE with Ag NPs features additional advantages such as stronger resistance to electrode fouling and improved electrocatalytic activity toward reductive dehalogenation. WEs decorated with Ag NPs are commonly employed in three main types of electroorganic reactions: dehalogenation,⁷⁵ carboxylation,⁷⁶ and reductive cross-couplings.^{77–81} Below are examples for each type of these reactions.

Electrochemical dehalogenation is a class of organic reaction that has important applications for decontamination of organic pollutants among other synthetic applications.⁸² This reaction involves formation of a radical intermediate as the result of a reductive cleavage of the C–X moiety. The resulting radical intermediate can (i) abstract a hydrogen atom directly from a suitable donor or (ii) reduce by one electron to form the corresponding carbanion and pick up a proton to form a C–H bond.^{83,84} In a seminal work, Isse et al. employed glassy carbon (GC) decorated with Ag NPs for the electrochemical dechlorination of benzyl chloride. The GC decorated with Ag NPs was prepared using potentiostatic electrodeposition with the potential of the WE stepped from 0.5 to -0.4 V vs Ag/Ag⁺

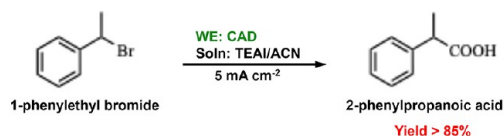
and held at -0.4 V at varying times (i.e., 30, 50, and 90 s). Shown in Figure 2A–F is the effect of the electrodeposition time on size and distribution of Ag NPs, confirming that electrodeposition is a facile method to control distribution and size of Ag NPs. Electrocatalytic properties of Ag NPs were examined with CV, confirming that decorating GC with Ag NPs significantly shifts the reduction of the potential of benzyl chloride to lower potentials and the magnitude of the potential shift increases consistent with increasing deposition time (Figure 2G–H). Controlled potential electrolysis was performed in the three-electrode divided cell with ACN containing 0.1 M TEAP and 10 mM benzyl chloride and GC modified with Ag NPs as the WE. Toluene was found as the main product at 60% yield, while hydrocinnamionitrile and benzyl alcohol were formed in smaller amounts (Scheme 1A). These results along with additional

Scheme 1. Reaction Scheme and Experimental Setup of (A) Electrochemical Dehalogenation of Benzyl Chloride, (B) Electrochemical Carboxylation of Benzyl Halide Derivates, and (C) Electrochemical Alkenylation of RAE and Vinyl Iodide

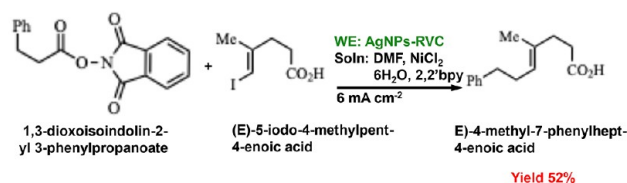
A) Electrochemical Dehalogenation of Benzyl Chloride (Isse et al.)



B) Electrochemical Carboxylation of Benzyl Halide Derivates (Yang et al.)



C) Electrochemical Alkenylation of RAE and Vinyl Iodide (Baran Group)



studies showed that the yield of dehalogenation reactions using GC decorated with Ag NPs exceeds that of pure Ag cathode and

decorating GC with Ag NPs forms an extremely stable WE that can be used for a preparative scale dehalogenation reaction for an extended period.⁷⁵

As mentioned earlier, another prevalent use of Ag NPs is electrochemical carboxylation via reductive cleavage of a C–X moiety to form a radical center.^{85,86} Several mechanisms for electrochemical carboxylation are suggested. The most prevalent mechanism includes a reductive cleavage of R–X and formation of the corresponding radical species. The radical center then reduces by one electron to generate the corresponding carbanion intermediate. Finally, the carbanion intermediate reacts with CO₂, fixing CO₂ by establishing a C–C bond. Yang et al. developed a compact Ag NP disk electrode for the electrochemical carboxylation of various benzyl halide derivatives. In this study, Ag NPs were prepared through the chemical reduction of Ag⁺ by hydrazine hydrate (10% V/V) at room temperature in an aqueous solution. Then, Ag NPs were separated from the solvent, thoroughly rinsed, and dried under vacuum. Finally, Ag NPs were compressed to form a 2 cm coin shaped electrode. The carboxylation experiment was conducted in a divided cell with 10 mL of ACN containing 0.1 M benzyl halide substrate and 0.1 M tetraethylammonium iodide (TEAI) using a compressed Ag NPs disk as the cathode and a Mg sacrificial anode. A compact Ag NP disk (CAD) electrode prepared with 20 nm Ag NPs shows 40% higher carboxylation yield compared with the Ag flake cathode. Moreover, authors reported an excellent electrolysis yield (i.e., >85%) and great electrode recyclability (i.e., up to 10 cycles) for carboxylation of seven benzyl halide derivatives using a CAD electrode (Scheme 1B).⁷⁶

The Baran research group demonstrated broad utility of coupling heterogeneous electrocatalysis with Ag NPs and homogeneous electrocatalysis with Ni-based complexes to carry out novel cross-coupling reactions.^{77–81} For instance, Baran and co-workers employed this strategy for electrochemical alkenylation using active ester (RAE) and vinyl iodide as the starting reagents. Electrosynthesis was carried out in DMF containing RAE, vinyl iodide derivative, NiCl₂·6H₂O, 2,2'-bipyridine, and AgNO₃ with an undivided cell using RVC and Mg as the WE and sacrificial anode, respectively. The optimization process was developed with 1,3-dioxoisindolin-2-yl 3-phenylpropanoate and (E)-5-iodo-4-methylpent-4-enoic acid as the starting reagents and (E)-4-methyl-7-phenylhept-4-enoic acid as the target product. It was shown that electrolysis

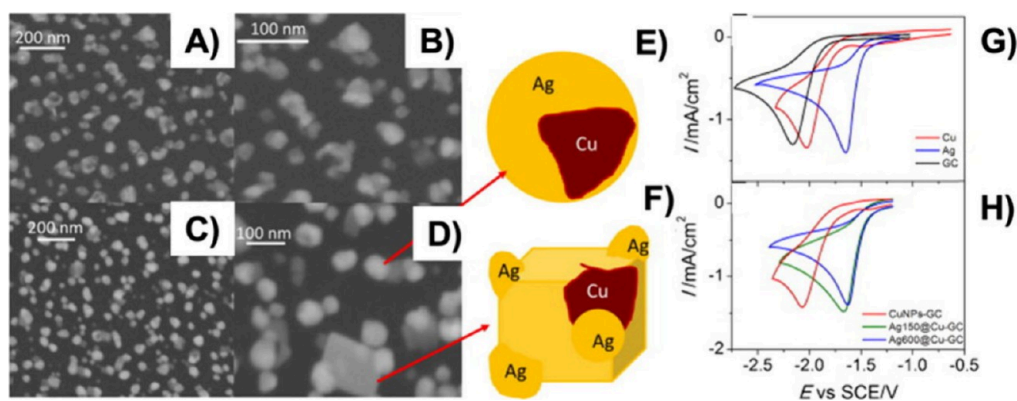


Figure 3. SEM analysis of (A, B) Ag150@CuNPs-GC and (C, D) Ag600@CuNPs-GC and (E, F) suggested decoration of Ag/Cu alloy NPs. (G) CV studies with (red) Cu, (blue) Ag, and (black) GC as cathode. (H) CV studies using GC decorated with (red) Cu NPs, (green) Ag150@Cu, and (blue) Ag600@Cu. Reprinted from ref 87. Copyright 2014 with permission from Elsevier.

affords 19% of (*E*)-4-methyl-7-phenylhept-4-enoic acid in the absence of AgNO₃, demonstrating the importance of Ag in carrying out the electroorganic reaction. Electrode characterization studies together with electroanalytical measurements indicated a reductive cleave of the NHPI ester and generation of the alkyl radical species mediated by electrodeposited Ag NPs at the RVC electrode. Electrosynthesis with pure Ag cathode or Ag-plated RVC featured yields of 20% and <5%, respectively, further indicating the importance of the Ag NPs for heterogeneous electrocatalysis and completing the cross-coupling reaction (Scheme 1C).⁷⁹

Ag has been employed in mixtures with other metals to make Ag–metal alloy NPs. In comparison with pure sample, Ag/metal NPs show improved electrocatalytic response toward electroreduction of C–X bonds. Durante et al. employed Ag–Cu alloy NPs deposited on a GC rod for the electrochemical cleavage of the C–Cl bond in a variety of organohalide compounds such as benzyl chloride and chloroacetonitrile. Cu NPs were first electrodeposited directly onto the GC electrode through a double potential step process which involves applying –0.65 V vs SCE for 1 s, followed by biasing electrode at –0.077 V vs SCE for another 20 s to allow growth of Cu NPs. The CuNPs-GC electrode was then placed into an aqueous solution containing AgNO₃ and potassium nitrate for 150 and 600 s, forming Ag–Cu alloy NPs with nominal composition of Ag150@Cu NPs-GC and Ag600@Cu NPs-GC, respectively. Structural characterization with SEM confirmed that Cu NPs are uniformly coated with Ag (Figure 3A–F). CV studies for the reduction of benzyl chloride with either Ag150@Cu or Ag600@Cu show a potential shift of >0.5 V vs SCE compared with unmodified GC, bulk Cu, and Cu NPs, confirming that electrocatalytic activities of Cu NPs are greatly enhanced by introducing a catalytic amount of Ag (Figure 3G, H). Moreover, electrochemical studies with chloroacetonitrile indicated that both Cu–Ag alloy NPs are showing better electrocatalytic performance compared to bulk Ag and Cu cathode, further confirming that electrocatalytic properties are enhanced by forming alloy NPs.⁸⁷

Besides Ag, a few other NPs, such as Pt,⁸⁸ Pd/Au,⁸⁹ Cu,⁹⁰ Pd/Cu,⁹¹ and Rh@CeO₂,⁹² have been employed for electroorganic transformation. However, as mentioned earlier, the major application of WEs modified with NPs is electrocatalytic activation of small molecules such as electrochemical CO₂ reduction (i.e., eCO₂RR). As such, there is an exciting overlap between this electrocatalytic reaction and electroorganic ones. Therefore, previous studies can provide extremely valuable lessons for selecting the most suitable NPs as well as the best approach for WE modification for targeted electroorganic transformations.

Finally, a crucial consideration for WE modification with NPs is the possible loss of electrochemical activity for large-scale applications or extended electrolysis. Decay of electrochemical performance can occur due to NP deactivation and a change in size. NP deactivation includes several mechanisms such as dissolution, passivation, formation of insulating oxide layer, poisoning with reactant or products of the organic transformation, and detachment from the WE. Moreover, the size of NPs increases due to a variety of routes such as aggregation or coagulation and Oswald ripening.⁹³

3. ELECTRODES MODIFIED WITH COMPOSITE MATERIAL

3.1. Composite Electrodes

Broadly, composite electrodes are a diverse family comprised of conductive materials present in dominant and subdominant phases affixed to the surface of the WE. These conductive materials, or composite materials, make it possible to access more extreme potentials that would otherwise be inaccessible with a pure substrate.

There are many types of composite materials, but for electrosynthetic applications, the most relevant are metal-based materials, chalcogens, and polymers. Composites can be further customized through structural or compositional modifications, resulting in changes in the functionality of the electrode. General properties may include heightened durability,⁹⁴ improved electrical conductivity,^{94,95} and introduction of electrocatalytic properties.⁹⁶ Heightened durability is brought about by the accumulation of composite materials, which lowers the rates of fouling, compositional change, and chemical degradation, allowing the electrode to withstand electro-synthetic reaction conditions. One of most prevalent structural modifications is the addition of conductive nanomaterials, which increases the active surface area of the electrode, improves conductivity, and regulates the electrocatalytic performance of the resulting material.

The following sections discuss examples of electrode modifications using various composite materials and their applications in electroorganic synthesis.

3.2. Examples of Composite Electrodes for Electroorganic Synthesis

3.2.1. Metal-Based Matrix Composites (MMCs). Metal-based matrix composites (MMCs) are a broad class of conductive materials used to prepare WEs. MMCs are further divided into subclasses of metal–metal (metal-MMCs) and metal–metal oxide matrix composites (metal-MOMCs). In metal-MMCs, the advantages of two or more metals (e.g., Cu and Pb) are combined by preparing a uniform composite to achieve an enhanced electrochemical and electrocatalytic performance. Metal-MMCs are commonly prepared through solvothermal methods or electrodeposition of metal layers.⁹⁷ Solvothermal methods consist of dissolving metal salts into a nonaqueous solvent and placing the solution under high temperatures and pressures. This promotes the combination of the metal particles and the matrix material into a uniform composite. The electrodeposition process deposits metal ions onto the matrix material through electrochemical methods.⁹⁸ Alternatively, metal-MOMCs are fabricated from homogeneous mixing of a metal (e.g., Pr) and a metal oxide (e.g., MnO₂). The resulting composition offers high electrocatalytic activity, electrochemical stability, and applications across large pH ranges. Metal-MOMCs are commonly prepared by hydrothermal methods, pyrolysis of the substrate material, or electrodeposition (e.g., Pr–MnO₂).⁹⁹ Hydrothermal methods proceed similarly to the solvothermal methods described above, except the reaction takes place in water or organic solvents while pyrolysis methods involve the decomposition of the material from the composite.⁹⁸ Despite the benefits seen with metal-MMCs and metal-MOMCs, they face challenges such as high production cost and processing requirements that require control during the fabrication process.

MMCs are often employed for the electrochemical activation of small molecules such as electrochemical HER⁹⁸ and

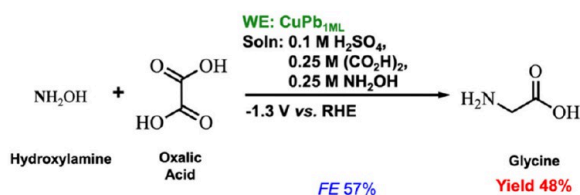
eCO₂RR¹⁰⁰ and as electrocatalysts for fuel cell applications.⁹⁷ However, despite their numerous advantages, MMCs have seldom been utilized for the electrosynthesis of small organic compounds. The following sections provide examples of these two subclasses of MMCs for electroorganic synthesis.

3.2.1.1. Metal–Metal Matrix Composites (Metal–MMCs).

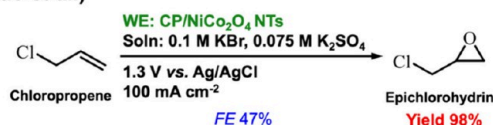
As previously described, metal–MMC composites are characterized by the mixing of two metals. These homogeneous metallic mixtures exhibit an electrochemical behavior that is greatly different from that of the pure metal substrate. This difference in the electrochemical response of a pure metal compared to its composite counterpart is rooted in various physical phenomena such as changes in the free energy of adsorption of reactants and intermediates and the synergistic effect of the neighboring metallic sites. Among various metals, Cu is widely used to make metal–MMCs. As such, Cu is known to show electrocatalytic properties for electroorganic reactions involving formation of the C–N bonds.^{99,101} However, electrosynthesis in acidic aqueous solutions at deeply reductive potentials using Cu electrodes suffers from low faradaic efficiency (FE) since HER is the dominant process.¹⁰² Creating a metal–metal composite is an effective strategy to utilize the electrocatalytic properties of Cu while minimizing the extent of HER. This strategy was employed by Broersen et al., where the development and use of a Cu–Pb composite, also referred to as CuPb_{IML}, for the electrosynthesis of glycine from oxalic acid and hydroxylamine sulfate in a divided cell containing 0.1 M H₂SO₄ was reported. The CuPb_{IML} WE was prepared with an underpotential deposition method, where a monolayer of Pb was deposited onto the Cu electrode. CuPb_{IML} WE features a 48% yield of glycine and FE of 57%, which is significantly higher than that of bare Cu and Pb (Scheme 2A).¹⁰³ CV studies showed

Scheme 2. Reaction Scheme and Experimental Setup for (A) Electrosynthesis of Glycine Using a Cu/Pb Composite and (B) Electrosynthesis of Epoxides Using a Ni/Co Oxide Composite

A) Electrosynthesis of Glycine (Broersen et al.)



B) Br radical-mediated electrosynthesis of ECH (Gao et al.)



the same amount of Pb was present on the freshly prepared CuPb_{IML} against the same electrode following preparative electrolysis, confirming excellent stability of the composite electrode (Figure 4A). Additional electrochemical and optimization studies showed that the Pb monolayer reorganizes into individual Pb islands on the surface of the Pb-doped Cu substrate. This rearrangement provides a unique electrocatalyst microenvironment where proton adsorption is drastically hindered, while production of glycine is enhanced (Figure 4B).

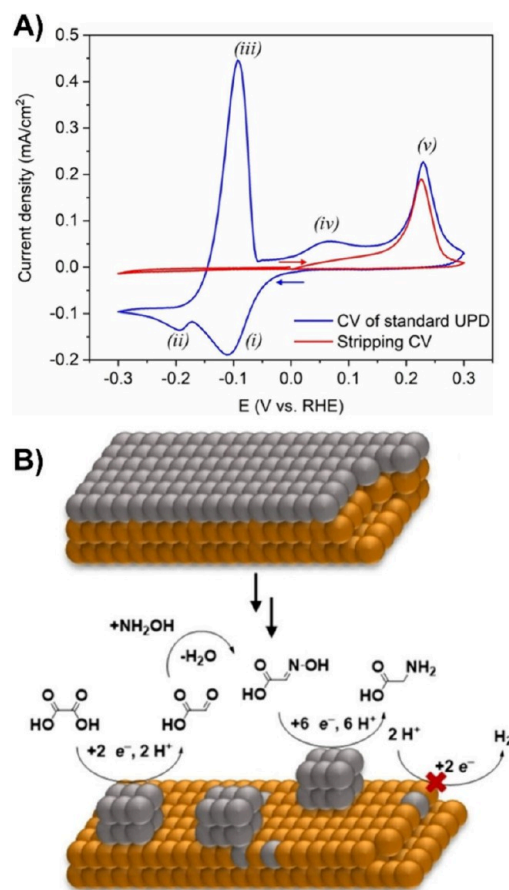


Figure 4. (A) Cyclic voltammograms of the typical deposition and stripping of Pb (blue) and the stripping of Pb from CuPb_{IML} in the absence of Pb (red). The peaks present are (i) the deposition of the monolayer, (ii, iii) the reduction and oxidation of Pb, and (iv, v) the stripping of the Pb. (B) Deposition of Pb monolayer on Cu substrate (top) and subsequent restructuring to expose Pb-doped Cu below (bottom). Pb and Cu are depicted by grey and orange spheres, respectively. Pb islands catalyze the reductions of oxalic acid and oxime to form glycine while inhibiting HER. Reprinted with permission under a Creative Commons CC-BY 4.0 from ref 103. Copyright 2023 Wiley & Sons.

3.2.1.2. Metal–Metal Oxide Composites (Metal–MOMCs).

In contrast with metal composites, metal–MOMCs have been more frequently employed for the electrosynthesis of small organic molecules. This class of materials exhibits higher chemical stability in harsh electrochemical reactions. Additionally, the redox behavior of metal–MOMCs can be tuned through structural modifications, such as modifying the metal-to-metal oxide ratio.^{104–108}

While various metal–MOMCs have been applied in organic electrosynthesis,^{104,105} composites of Ni and Co oxide (Ni_xCo_{3-x}O₄) are some of the most prevalent.^{106–108} For example, Gao et al. decorated NiCo₂O₄ with nanotips (NTs) on carbon paper (CP) and employed it as a promising candidate for Br radical-mediated electrosynthesis of epichlorohydrin (ECH) from chloropropene. The CP/NiCo₂O₄ electrode was formed through hydrothermal calcination of NiCl₂·6H₂O, CoCl₂·6H₂O, urea, and CP in an autoclave at 120 °C for 12 h. Electrolysis was carried out in a single-chambered cell using CP/NiCo₂O₄ as the WE in the presence of 0.1 M KBr and 0.075 M K₂SO₄ as the solvent-supporting electrolyte. This electrosynthetic scheme was employed for the conversion of 14 additional olefins to their

corresponding epoxides, generally presenting yields of >85% (Scheme 2B). In addition to their success in those numerous reactions, the NTs demonstrated strong consistency when employed for 30 cycles, displaying relatively unchanged yields and FEs (Figure 5A).¹⁰⁹

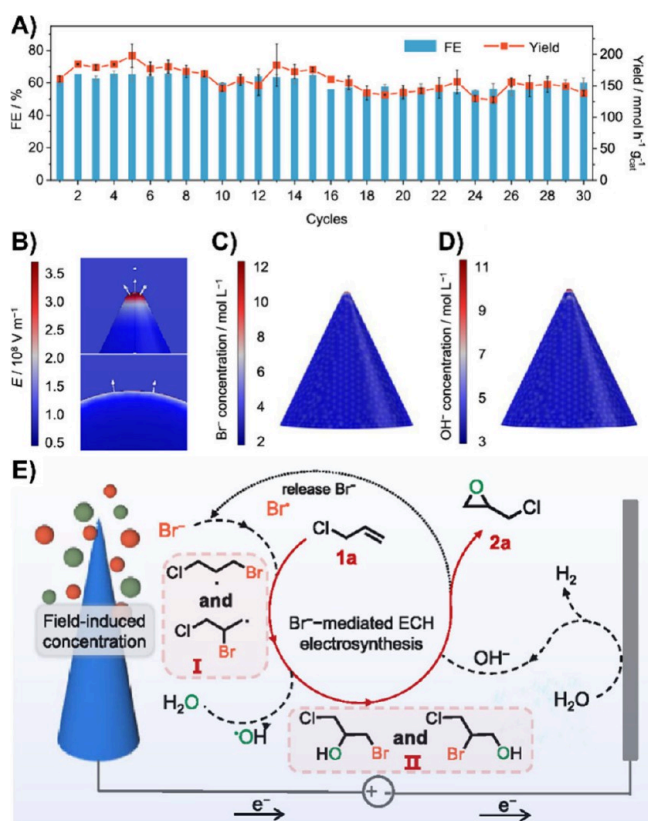


Figure 5. (A) NiCo₂O₄ NT FE and yield for epoxide formation across 30 cycles. (B) Electric field of NiCo₂O₄ samples with tip radii of 2 (top) and 40 nm (bottom). (C) Br[−] and (D) OH[−] surface concentrations at NiCo₂O₄ NTs. (E) Proposed reaction mechanism for Br-mediated electrocatalytic hydrogenation of ECH using the NiCo₂O₄ electrode. Bromine is depicted in red while oxygen is depicted in green. Adapted with permission from ref 109. Copyright 2024 American Chemical Society.

Extensive optimization studies also showed that the presence of both anions and the nanotip is crucial for high-yield electrocatalysis. Finite element (FEM) simulations were employed to further shed light on the correlation of the nanosized tip geometry and anion concentration (Figure 5B). Based on the FEM studies, incorporation of high-curvature NTs enhanced the magnitude of the electric field near the WE, resulting in the formation of an enrichment layer where concentrations of OH[−] and Br[−] anions were greatly enhanced (Figure 5C, D). From these studies, a detailed reaction mechanism, including the role of the anions in the conversion of olefin to epoxide, was proposed (Figure 5E).

3.2.2. Metal–Chalcogenide Composites. Metal chalcogenides are a class of inorganic compounds in which metal components are surrounded with a chalcogen motif (e.g., S and Se) in a specific stoichiometric ratio.¹¹⁰ While these compounds can be challenging for electrode design as their electrical conductivity is strongly dependent on composition,¹¹⁰ they still have been vastly employed for various electrochemical studies.¹¹¹ Some metal–chalcogenide electrode designs offer large surface area, rapid ion transfer, high electrical conductivity,

and enhanced electrocatalytic activity.¹¹¹ The modifiable nature of metal–chalcogenide composition and their compatibility with other constituents allow for the reduction of their inherent limitations, improving their utility as electrode materials.^{111,112} Other properties can be further tuned by enhancing the surface area of the material with NPs or other organic motifs. Matrixing with other materials can also prevent the aggregation of the chalcogenides.¹¹² Similar to MMCs, composites of metal–chalcogenide are usually prepared through hydrothermal, solvothermal, or electrodeposition methods.¹¹³

Metal chalcogenides have been applied to electroorganic conversions both as the sole modification and in concert with additional modifications. As the substrate in electroorganic reactions, sulfide-based metal chalcogenides have been among the most commonly utilized.^{114–117} A great example is a report by Huang et al., where carbon cloth (CC) modified with MoS₂ was employed for selective electroreduction of furfural (FFA) to furfuryl alcohol or electro-dimerization to form hydrofuroin.¹¹⁸ Preparation of the composite WE is shown in Figure 6A. In summary, MoCl₅, DMF, thioacetamide, and a small piece of CC were heated at 200 °C in an autoclave for 24 h. The heating step results in uniform growth of MoS₂ onto the CC substrate (i.e., MoS₂/CC). Additional annealing of MoS₂/CC at 100, 150, 200, and 250 °C results in formation of WEs named M150, M200, and M250, respectively (Figure 3A). Preparative scale electrolysis was performed using annealed MoS₂/CC WE with a divided cell containing either 0.4 M sodium acetate (pH = 3), 0.4 M sodium phosphate (pH = 6), or 0.4 M sodium borate buffer (pH = 9). Product distribution analysis indicated that furfuryl alcohol synthesis was enhanced at −1.2 V vs Ag/AgCl with the M100 electrode resulting in a selectivity of 94.4% and conversion yield of 34%. Highest selectivity for the formation of hydrofuroin was observed at −1.0 V vs Ag/AgCl with the M250 electrode.

Extensive material characterizations were employed to study the correlation between the structure and the electrocatalytic activity. It was shown that MoS₂ exists as a highly conductive octahedral (1T) or semiconductor hexagonal (2H) structure depending on sulfur atom arrangement with 1T transforming to 2H arrangement by merely changing annealing temperature. Further computational studies indicated that these structural arrangements feature unique control over product selectivity between electrocatalytic hydrogenation and dimerization by favoring reaction intermediates. As such, the relative free energies studies indicated that electroreduction to furfuryl alcohol is more energy efficient on a 2H-MoS₂ electrode (Figure 6B). In contrast, electroreduction is slightly inhibited on 1T-MoS₂ while electro-dimerization is promoted due to favorable adsorption of the reaction intermediates onto sulfur moieties (Figure 6C).¹¹⁸

3.2.3. Polymer Composites. In polymer composites, conductive polymers are combined with metals or other semiconductors to form a new material that exhibits enhanced electrocatalytic performance. NPs, both metal (e.g., Au, Cu, Ni) and semiconductor (e.g., MnO₂), are a common choice for their synergistic properties which provide excellent electrochemical stability and conductivity when embedded in a conductive polymer matrix (e.g., polypyrrole).¹¹⁹ Different approaches have been employed to prepare polymer composites.¹²⁰ A common route is the one-step coelectrodeposition of NPs dispersed in a solution with a monomer which is then polymerized and deposited together.¹²¹ While the one-step process is simple, it

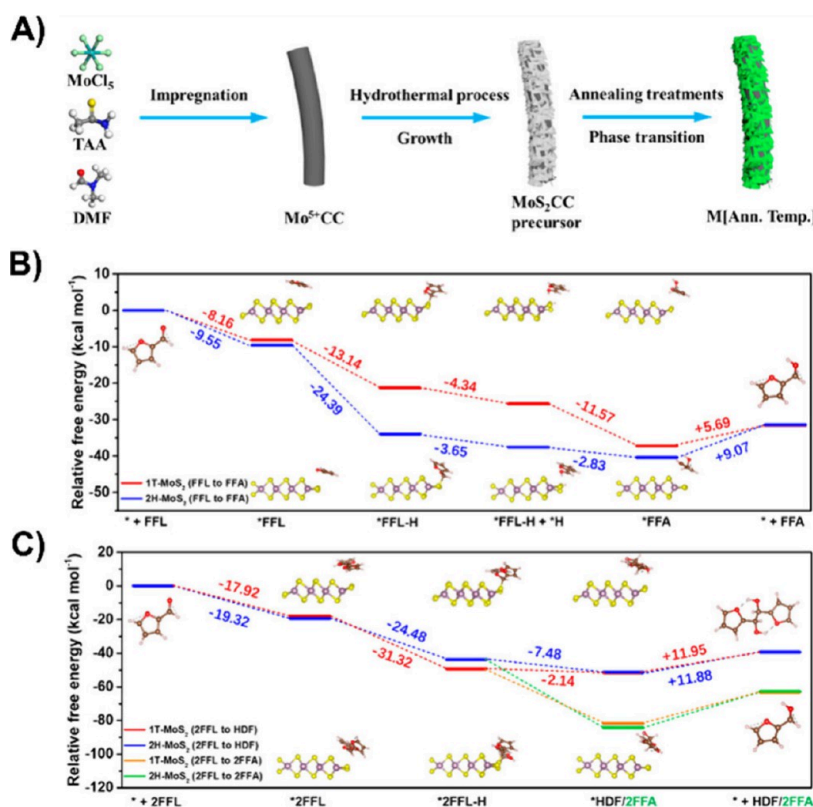


Figure 6. (A) Schematic detailing the fabrication of MoS₂-based electrode. Free energy diagrams of (B) hydrogenation process, and (C) electro-dimerization on different modeled MoS₂ surface. Adapted with permission from ref 118. Copyright 2022 American Chemical Society.

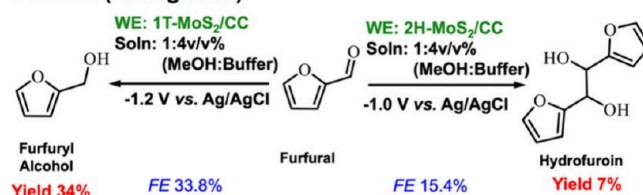
does pose the risk of NP agglomeration, thus limiting the effectiveness of the modification.

Conductive polymers' π -electron-conjugated structures, such as polyaniline (PANI), are an especially popular choice for the preparation of the conductive matrix.^{122,123} Polymer composites are compelling choices, as introducing a certain amount of metal or other alterations to the conductive polymer backbone can lead to the formation of new materials with enhanced electrocatalytic activity and greater structural support.^{119,124} However, polymer composite electrodes can be quite complex to design with many properties influencing their performance. Some drawbacks of WEs modified with polymer composites include NP agglomeration, poor reproducibility, and high cost of electrode preparation.¹²¹ Additionally, detailed mechanistic understanding using these complex electrodes is particularly difficult. WEs decorated with polymer composites are commonly used in eCO₂RR,¹²² HER, OER, oxidation of alcohols (e.g., methanol and ethanol), and devices such as sensors and supercapacitors.¹²⁴ Despite their versatility as electrode materials and vast application in the electrochemical activation of small molecules, there are limited reports on the use of polymer composites for organic electrosynthesis.

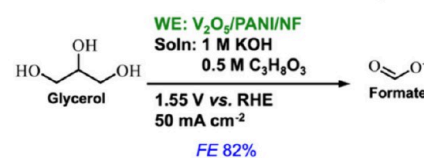
Valorization of glycerin through selective and efficient electrooxidation (i.e., GOR) requires precious metals and use of large anodic potentials.^{125,126} Wu et al. reported developing a polymer composite WE consisting of vanadium oxide (V₂O₅)/polyaniline (PANI)/nickel foam (NF) for selective electro-oxidation of glycerol to formate (Scheme 3B). The process of developing the polymer composite WE includes the electrodeposition of PANI onto NF followed by the electrodeposition of V₂O₅ onto the PANI matrix (Figure 7A). Electrooxidation of glycerol was carried out in a three-electrode cell containing 1 M

Scheme 3. Reaction Scheme and Experimental Setup of (A) Electrocatalytic Hydrogenation and Dimerization of Furfural Using MoS₂ on CC and (B) Glycerol Oxidation to Formate Using PANI-Based Composite

A) Electrocatalytic Hydrogenation and Dimerization of Furfural (Huang et al.)



B) Glycerol Oxidation Reaction to Formate (Wu et al.)



KOH and 0.5 M glycerol with V₂O₅/PANI/NF WE. In comparison with V₂O₅/NF and PANI/NF, V₂O₅/PANI/NF displayed drastically improved electrocatalytic performance toward GOR. Computational studies along with experimental results confirmed that among other conductive polymer matrixes, PANI features the least amount of free energy for H⁺ adsorption, thereby creating the most alkaline environment for production of formate (Figure 7B and C). In tandem with the role of PANI, GOR is further enhanced by the presence of V₂O₅ as the polarity of the catalyst matches that of glycerol (Figure 7D).¹²⁷ Together, PANI and V₂O₅ feature a synergy in which

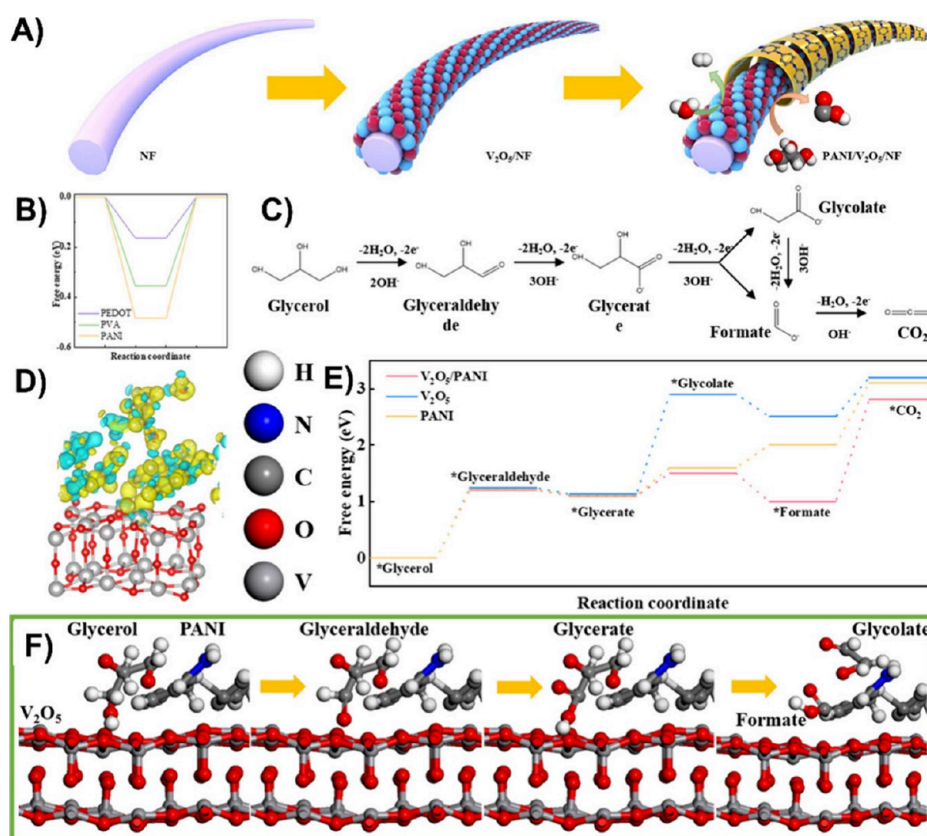


Figure 7. (A) Illustration of a V_2O_5 /PANI/NF electrocatalyst assembly, (B) calculated free energy for H^+ adsorption, (C) proposed reaction mechanism for GOR to formate in alkaline solution, (D) charge density difference in a V_2O_5 /PANI model with glycerol with charge accumulation in light blue and depletion in yellow, (E) free energy diagram of GOR with different WEs, and (F) proposed mechanism of V_2O_5 /PANI regulation in GOR. Adapted with permission from ref 127. Copyright 2024 American Chemical Society.

simultaneous local pH control by PANI and facile adsorption of reaction intermediates onto V_2O_5 promotes GOR while further preventing excess oxidation to CO_2 (Figure 7E and F).

4. ELECTRODES MODIFIED BY REDOX AND CONDUCTIVE POLYMERS

4.1. Polymer-Modified Electrodes

In polymer-modified electrodes (PMEs), the polymeric material is deposited onto a conductive substrate to make a modified WE. Unlike the electrochemical properties of metals, those of polymers can be finely tuned through various methods such as altering the composition of the monomeric unit, introducing various redox-active moieties or molecular electrocatalysts, and incorporating copolymers to enhance electrical conductivity or induce antifouling properties.^{128–130} The ability to manipulate chemical and electrochemical properties through structural modifications is one of the astonishing characteristics of WEs modified with polymers, enabling PME to be employed in a variety of electrochemical applications such as electrochemical sensors,^{131,132} fuel cells,¹³¹ energy storage,¹³³ and supercapacitors.¹³⁴

Closer to the topic of this Review, PME were widely employed for electrochemical reactions (e.g., HER,^{135–137} OER,^{138–140} and eCO_2RR ^{141–143}) using either redox polymers or conductive polymers. In the following paragraph, we introduce conductive and redox polymers. Next, we provide a brief discussion for WE modification with each category of

polymers. Finally, we examine a few recent examples of the use of each category in electroorganic reactions.

4.2. Redox and Conductive Polymers for Organic Electrosynthesis

4.2.1. Redox Polymers. Redox polymers contain electroactive sites that feature a reversible electrochemical behavior. In these polymers, redox reactions allow electrons to hop from one redox-active center within the polymer to the next site until the charge finally arrives at the interface of the WE and solution. Redox polymers show totally reversible electrochemical behavior in the absence of any analyte as both the oxidized and reduced forms of the redox center are stable.³² Classification of redox polymers is a function of the location and nature of the redox center as well as the nature of the polymer backbone. In terms of the nature of the backbone, redox polymers can have a conjugated backbone that exhibits very good electrical conductivity or a nonconjugated backbone where the backbone merely connects redox-active monomers, making electron hopping between redox-activated sites the sole mode of conductivity.^{131,144} Moreover, the active site in redox polymers can adopt a range of options from outer sphere redox species (e.g., ferrocene) as pendant groups to organic redox pendants (e.g., nitroxyl, carbonyl, viologens).¹³¹ In this context, depending on the oxidation state of the polymer, different chemical and electrical properties are enhanced.¹⁴⁵

Redox polymers are deposited onto the WE through chemisorption or physisorption of the premade polymer.¹⁴⁶ Chemisorption is accomplished by graft-to or graft-from approaches.^{146–148} In the graft-to approach, chemisorption

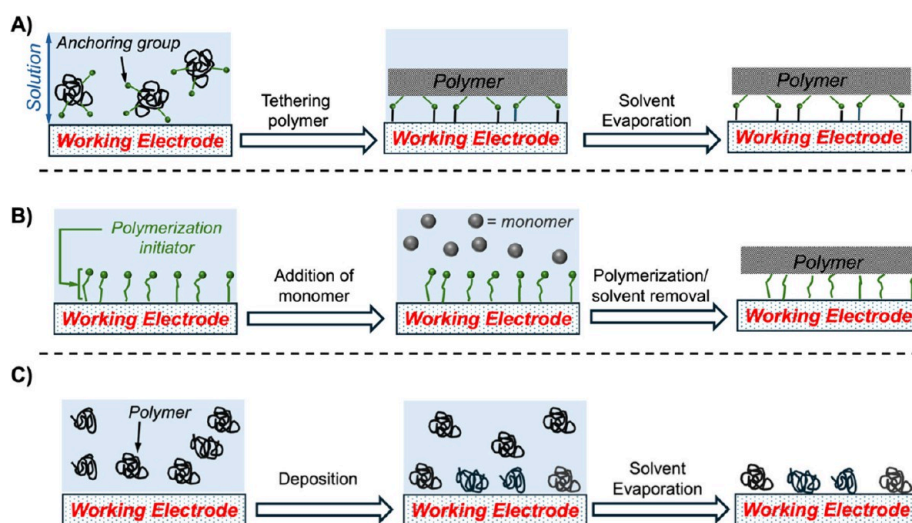


Figure 8. Methods for depositing redox polymer onto WE, including (A) graft to, (B) graft from, and (C) physisorption. With the graft-to-electrode method, electrode modification includes tethering polymer onto the WE and solvent removal. In the graft-from method, initiator is covalently attached to the WE. Next, monomer is added to the WE. After polymerization is finished, solvent is removed. In the physisorption approach, polymer is added to the WE, and solvent is removed.

involves anchoring the polymer to the WE surface through a coupling reaction between a specialized functional group (e.g., thiols/disulfides) and substrate (e.g., C, Au, Si) (Figure 8A).^{146,149} In the graft-from approach, a polymerization initiator (e.g., 2-bromoisobutyrate)¹⁵⁰ is covalently immobilized onto the WE surface (e.g., C, Si, Ag), and polymeric chains are grown through addition of monomers (Figure 8B).¹⁵¹ Alternatively, physisorption involves applying a polymer to the electrode surface using various methods such as drop casting, dip coating, spin coating, and spray coating. The modification with each of these methods usually involves application of wet polymer to the WE and the solvent evaporation (Figure 8C).

Selection of the polymer adhesion method relies heavily on the type of polymeric unit, surface area of the WE, ionic strength of the solvent, charge state of the polymer, and type of functional groups of the polymer. A general consideration is that physisorption is generally simpler and regarded as a weak, reversible process, whereas chemisorption offers stronger binding between substrate and coating layer and is an irreversible process.¹⁴⁶ Therefore, WEs modified with physisorbed polymers exhibit lower chemical and electrochemical stability compared with the chemisorbed method.

One of the most versatile electrocatalysts for electrochemical C–H activation is 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO).^{152–154} However, TEMPO shows low chemical stability and relatively low turnover frequency (TOF) when employed as a freely diffusing homogeneous electrocatalyst. The poor chemical stability and low TOF have shown to be substantially improved by incorporating TEMPO into a polymeric backbone, forming TEMPO–redox polymer, which has been employed vastly for electrooxidation of alcohols and electrochemical C–H activation.^{155–158} A very good example is a report by Hickey et al. where TEMPO was tethered onto linear polyethylenimine (LPEI) via covalent immobilization using glycidyl linkage, forming TEMPO–LPEI that is then cross-linked with glutaraldehyde onto the GC electrode. Finally, multiwalled carbon nanotubes (MWCNTs) were added to GC modified with TEMPO–LPEI to improve the electrochemical stability of the resulting electrode in water. Modified GC with TEMPO–LPEI–MWCNT was employed for electrooxidation

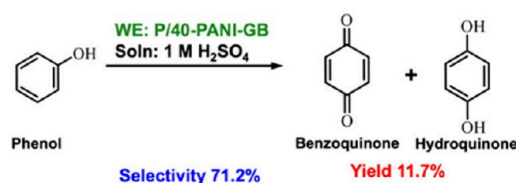
of saccharides and short-chain alcohols (Scheme 4A).¹⁵⁹ Electrolysis was carried out in an aqueous buffer containing

Scheme 4. Reaction Scheme and Setup for (A) Electrooxidation of Various Saccharides and Short-Chain Alcohols Using TEMPO–LPEI–MWCNT-Modified GC and (B) Electrooxidation of Phenol Using PANI-Modified GB

A) Electrooxidation of Saccharides and Short Chain Alcohols (Hickey et al.)



B) Electrooxidation of Phenol (Han et al.)



0.2 M phosphate/citrate at a constant potential of 0.8 V vs SCE using a three-electrode cell with GC modified with TEMPO–LPEI–MWCNT as the WE. These modifications prompted enhanced structural rigidity and greatly enhanced the active surface area. As shown in Figure 9, WE-modified TEMPO–LPEI–MWCNT displayed greater anodic current density and higher electrooxidation compared to the condition where 4-methoxy-TEMPO was employed as a homogeneous electrocatalyst. The difference in electrooxidation yield is attributed to the high localized abundance of amines from the LPEI backbone which serve as a base that is essential for completing electrooxidation with TEMPO. Moreover, TEMPO–LPEI facilitates rapid diffusion of the substrate and a greater localized buffer region through the polymer network, which further facilitate electrocatalytic activity of the modified WE.

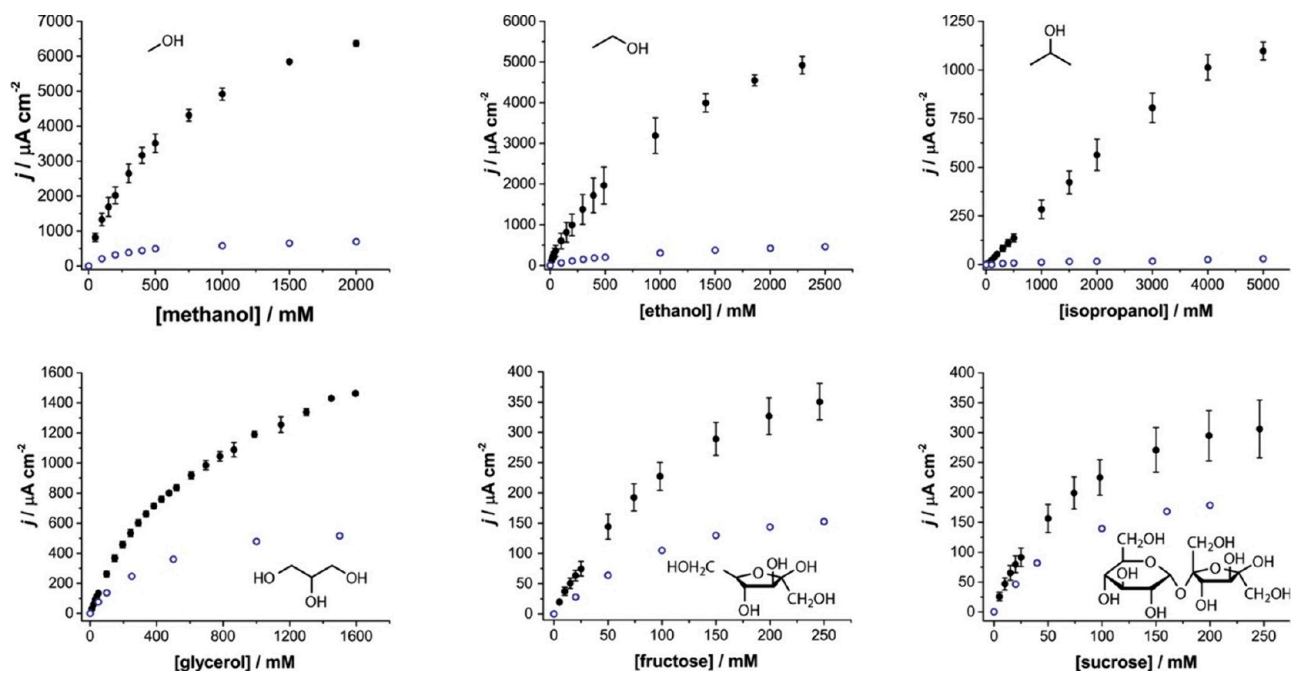


Figure 9. Electrochemical response of WE modified with cross-linked TEMPO-LPEI films (●) and 2.5 mM 4-methoxy-TEMPO (○) for methanol, ethanol, isopropyl alcohol, glycerol, fructose, and sucrose. Reprinted with permission from ref 159. Copyright 2015 American Chemical Society.

4.2.2. Conductive Polymers. Conductive polymers (CPs) are characterized by a π -conjugated backbone, which allows for the flow of electrons along the polymer structure. In CPs, monomers are connected via an extensive network of alternating single- and double-bonded hybridization, giving rise to metal-like electrical conductivity.¹⁶⁰ Additional properties of CPs include totally reversible redox behavior, large reactive surface area, ease of synthesis, and adjustable chemical structures.^{161,162} There are various strategies to modify a WE with CPs for organic electrochemistry.^{163–165} In most cases, the electrode is coated with various types of CPs such as polypyrrole (PPy), PANI, poly(3,4-ethylenedioxythiophene) (PEDOT), and polythiophene (PTh).¹⁶⁶ However, there have been several reports in which the electrocatalyst was directly electropolymerized onto the WE as a conductive polymer.^{167–169}

The most common route for affixing a conductive polymer onto a substrate is electropolymerization through oxidation or reduction of monomers. Electropolymerization is generally achieved by using galvanostatic or potentiostatic methods. An explanation of each method is provided in Section 2.1. The general procedure for reductive electropolymerization is shown in Figure 10. During electropolymerization, organic monomers are oxidized or reduced at the electrode surface, forming soluble oligomers that saturate the electrode interface. Following the saturation stage, electrosynthesized oligomers deposit onto the WE, forming initial nucleation sites for the polymerization stage. In the final stages of electropolymerization, the growth of the polymer occurs on these nucleation sites.¹⁶⁰ It should be noted that oxidative polymerization also includes these general steps and selection between reductive and oxidative polymerization depends on the monomer.¹⁶⁶

The extent of electropolymerization is a function of various parameters such as applied electrical current or electrochemical potential, deposition time, and monomer concentration.^{170,171} Conductive polymer modifies WEs on various levels, ranging from isolated polymeric islands to a consistent multilayer polymeric film.¹⁷¹ An electropolymerized layer may contain

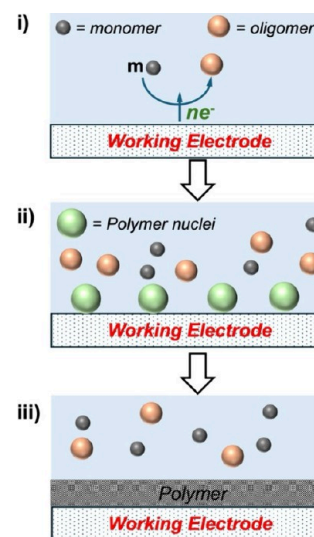


Figure 10. Reductive electrodeposition of conductive polymer onto the WE including (i) reduction of monomer to oligomer, (ii) saturation of the diffusion layer with oligomer and polymer nucleation, and (iii) formation of a polymer layer onto the WE.

longer chains and cross-linked materials. It is important to note that stability of conductive polymers increases as a function of chain length.^{141,142} Electropolymerized film has great adhesion to the WE. However, enhanced polymer adhesion makes additional modification of the electropolymerized layer difficult. Another drawback of electropolymerization is poor reproducibility where WEs modified with identical electrochemical methods usually exhibit different electrochemical properties.¹⁶⁰ Alternatively, chemical polymerization can be utilized to improve reproducibility and allow for post-modification. With chemical polymerization, the polymer is synthesized in the solution phase, and then external application methods such as drop casting are employed to modify the WE.

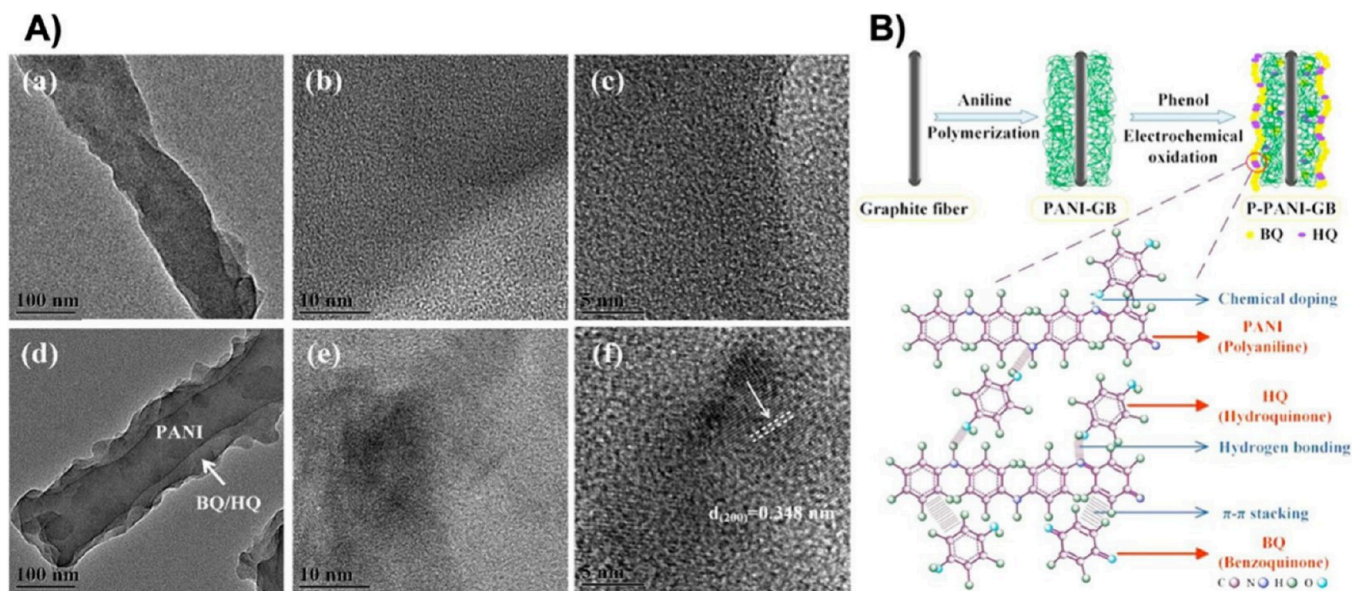


Figure 11. (A) High-resolution transmission electron microscopy (HR-TEM) images of PANI-GB (a–c) and P/40-PANI-GB (d–e). (B) Simplified representation of graphite fiber modification with PANI and interaction of graphite-PANI WE with HQ during electrooxidation. Reprinted from ref 177. Copyright 2018 with permission from Elsevier.

CPs are prevalent in energy storage,¹⁷² energy conversion, electrochemical sensors, CO₂ reduction, O₂ reduction, and nitrate reduction.¹⁷³ As such, CPs have been extensively employed for organic electrosynthesis. A few recent examples include use of poly(pyrrrole-viologen),¹⁷⁴ thiophene polymers functionalized with alkyl chains,¹⁷⁵ poly-3,4-diaminobenzoic acid (PDABA),¹⁷⁶ TEMPO-modified polyaniline (PANI),¹⁷⁷ and ferrocene-modified CP as efficient heterogeneous electrocatalysts for various electroorganic transformations.^{168,169}

Besides their electrocatalytic properties, CPs can be utilized to protect WEs against fouling and maintain their electrochemical performance. In summary, during electrosynthetic reactions, small organic molecules tend to deposit onto the WE and counter electrode (CE), passivating either or both electrodes. Electrode passivation simply leads to a loss of electrochemical activity. Therefore, protecting WEs against fouling and deactivation is crucial for practical and large-scale electrosynthetic purposes. As such, Han et al. report electrooxidation of phenol to benzoquinone/hydroquinone (BQ/HQ) on an electropolymerized PANI graphite brush electrode (PANI-GB). PANI was electrodeposited onto GB by using a potentiostatic method. High-resolution transmission electron microscopy (HR-TEM) analysis indicated that GB is uniformly decorated with PANI (Figure 11A(a–c)). Electrooxidation of phenol to benzoquinone (BQ)/hydroquinone (HQ) was employed by performing successive cyclic voltammetry studies in 0.1 M NaCl solution containing 0.5 g L⁻¹ phenol from -0.2 to 1.0 V at a scan rate of 5 mV/s. Electrodes obtained following the electrooxidation experiment were named P/*n*-PANI-GB with *n* indicating number of cycles where electrooxidation CV was executed.¹⁷⁷ Electrochemical performance of P/*n*-PANI-GB increased with increasing electrooxidation, reaching a 16% yield of phenol electrooxidation and 71% selectivity toward formation of BQ/HQ with P/40-PANI-GB (Scheme 4B). HR-TEM studies together with additional electrochemical measurements revealed that electrogenerated BQ/HQ forms a thin layer onto PANI (Figure 11B(d–e)) through π stacking (Figure 11B). In

this context, PANI prevents direct electrodeposition of BQ/HQ onto the GB directly, thereby preventing electrode passivation.

Finally, it is important to consider a few drawbacks that are associated with WE modification using polymers. For both types of polymers, adhesion and stability are still a problem, as the polymeric film tends to partly detach from the WE or dissolve in the solvent when employed for extended electrolysis or subjected to high solvent flow. Electrochemical performance as well as electrical conductivity decays due to the loss of physisorbed redox molecules, especially in large-scale applications. Moreover, creating a polymer film with uniform thickness and consistent chemical properties on large electrodes or porous substrates is still a technical challenge for future research.

5. ELECTRODE MODIFICATION WITH MATERIALS BASED ON ORGANIC FRAMEWORKS

5.1. Materials Based on Organic Frameworks

Materials made of organic frameworks exhibit common properties such as high degrees of porosity, high surface area, and crystallinity.^{15,178} These materials have been employed for various electrochemical applications. For organic electrochemical applications, metal organic frameworks (MOFs) and covalent-organic frameworks (COFs) have mainly been employed to modify the WE. This section briefly discusses the use of MOF- and COF-modified electrodes for organic electrosynthetic reactions.

5.2. Electrodes Modified with Metal Organic Frameworks

Metal organic frameworks (MOFs) are a class of materials wherein a metal center is coordinated with an organic ligand linker, forming a porous and highly crystalline structure.¹⁵ Several parameters determine functionality and behavior of MOFs such as the type of metal (e.g., *d*-block, lanthanide), the redox state of the metallic center, and the chemistry and structure of the organic ligand. Owing to the structural flexibility and high chemical and thermal stability,¹⁷⁹ MOFs have been used in various applications such as gas storage, drug delivery,

rechargeable batteries,¹⁸⁰ and photoswitches.¹⁸¹ The first examples of MOFs were considered insulators due to low electrical conductivity. However, in the past few years, the issue of conductivity of MOFs has been addressed through various strategies, such as the incorporation of conjugated linkers, mixed valence metal ions, or electroactive guest species.¹⁸²

In tandem with the emergence of conductive MOFs, the electrochemical application of these materials also gained momentum. MOFs are generally synthesized by linking organic and inorganic linker units, forming 3D structures with well-defined pore sizes. Usually, a MOF-modified WE is made during a two-step process that involves the synthesis of the framework and subsequent application onto the substrate. The synthetic procedures for MOFs are incredibly variable, ranging from numerous wet synthesis procedures to electrochemical or sonochemical approaches.¹⁸³ Several methods were developed to create a thin layer of MOFs on the WE, including solvothermal, hydrothermal, drop-casting, dip-coating, and spin-coating of the synthesized frameworks onto the substrate.¹⁸⁴ For example, nanoporous materials are synthesized through nucleation and then organic–inorganic crystal formation through aggregation with the surface-absorbed organic molecules. Alternatively, atomic layer deposition has been employed to form films of metal precursor on the electrode which were then reacted with the organic linkers to produce the framework.¹⁸⁵

A myriad of properties make MOFs desirable for electrochemical applications including the reduction of small molecules, such as CO₂ and nitrate,^{185,186} sensors,¹⁸⁷ and electroorganic synthesis. First, MOF-modified electrodes offer unique characteristics that are crucial for electrochemical applications such as large surface areas and high porosity.¹⁵ Second, MOF-modified WEs show unique stability under electrochemical working conditions, making them useful for various electrocatalytic applications.¹⁸⁸ Finally, the mechanical features (e.g., pore size, structure, and topology) along with electrochemical properties of MOFs can be tuned through pre- and post-synthesis processes to fabricate the WE with desired properties.¹⁵

Recently, MOF-modified electrodes have received much attention for the electrosynthesis of small molecules such as electrooxidation of alcohols and electrosynthesis of the N–N bond.^{189,190} A very interesting example, however, is utilizing the MOF as an electrocatalyst for the electrodimersation of acrylonitrile (AN) to adiponitrile (ADN). Electrosynthesis of ADN, known also as the Baizer process, is a well-known electrochemical method to form raw material for Nylon-66 and various other polymeric products at the industrial scale.^{7,191–193} This electrodimersation occurs at deeply reductive potentials in acidic solution where HER is the dominant process. As a result, a Pd or Cd cathode is employed to minimize HER and enhance the yield of the electrosynthesis. Wang et al. showed that modifying Pb foil with Pb, PbO, and benzenedicarboxylate-based linkers (Pb-bdc MOF) forms an outstanding WE for electrodimersation of AN to ADN. The Pb-bdc MOF was carbonized using heat treatment at 600–900 °C forming different types of MOFs that are referred to as Pb-bdc-600 to -900 (Figure 12A). Extensive structural studies showed that as the result of thermal treatment of Pb-bdc MOF, Pb and PbO moieties are uniformly distributed across the MOF matrix (Figure 12B–E). The carbonized MOF suspension was drop-casted onto a Pb foil electrode and dried before electrochemical experiments. Extensive electrochemical measurements were

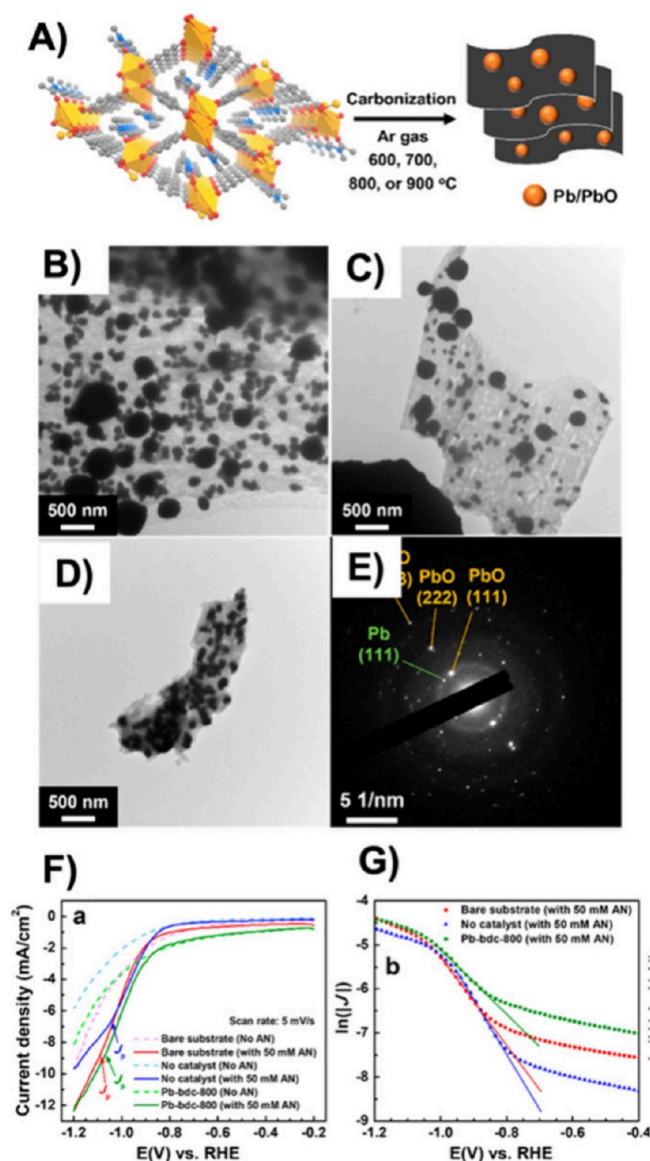
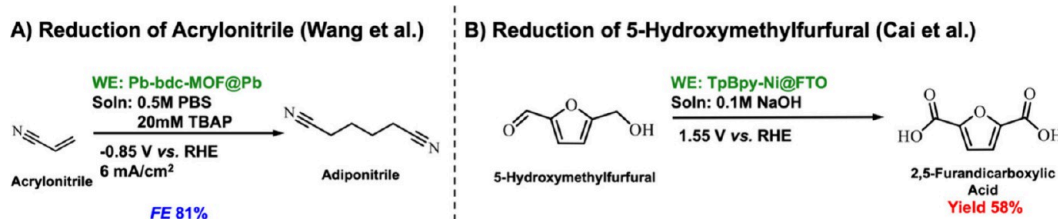


Figure 12. (A) Preparation of an electrically conductive MOF via thermal treatment. Pb, O, C, and N are shown with yellow, red, gray, and blue spheres, respectively. TEM characterization of (B) Pb-bdc-700, (C) Pb-bdc-800, and (D) Pb-bdc-900. (E) SAED data. (F) Linear sweep voltammetry (LSV) studies and (G) corresponding Tafel plots. Reprinted with permission from ref 194. Copyright 2024 American Chemical Society.

employed to investigate both HER and electrocatalytic AN dimersation (Figure 12F and G). These studies proved that Pd foil modified with MOF significantly suppresses HER while promoting greater cathodic response for the electrodimersation of AN. Preparative-scale electrosynthesis of ADN was carried out in a three-electrode cell containing 0.5 M PBS, 0.6 M AN, and 20 mM TBAP. Pd foil modified with the MOF electrode displayed a current density of 6 mA/cm², a minimum of threefold greater than others reported in the literature. Moreover, electrolysis with a Pd-MOF layer was carried out at −0.85 V vs RHE and affords FE of 67%. In contrast, electrolysis with Pd foil was carried out at −1.5 V vs RHE and yielded lower reaction yield (Scheme 5A).¹⁹⁴ These results together show the efficacy of modifying Pd foil with MOF to induce additional

Scheme 5. Reaction Scheme and Experimental Setup of (A) Electroreduction of Acrylonitrile Using Pb-bdc-MOF-Modified Pb Electrode and (B) Electroreduction of HMF Using TpBpy-Ni Deposited on Fluorine-Doped Tin Oxide, a COF-Modified Electrode



electrocatalytic properties while minimizing competitive undesirable processes like HER.

5.3. Electrodes Modified with Covalent–Organic Frameworks (COFs)

Covalent–organic frameworks (COFs) are made of an extended organic polymer network with rigid backbones.¹⁹⁵ COFs are similar to MOFs in terms of several structural features such as crystallinity and porosity.^{178,196} However, metallic components are less frequently employed in the structures of COFs. In contrast with linear polymers, COFs are a combination of planar monomers with additional chemical bonds and covalently linked bonds, leading to generation of two- or three-dimensional atomic layers.¹⁹⁶ 2D COFs (e.g., hexagonal, tetragonal) usually have π – π stacking interactions which hold each layer together and contain π -conjugated electron rich units. They contain organic backbones that are covalently linked in a sequential way. Alternatively, 3D-COFs are based on sp^3 -hybridized carbon or silicon atom center with tetrahedral confirmation, connecting monomers to form an extended network.¹⁹⁷ COFs offer tunable pore size, great chemical stability, and large surface area, which are important to ensure many catalytically active sites.¹⁹⁵ COFs are synthesized by using solvothermal condensation reactions or sonochemical means. Generally, COFs are stamped or dispersed onto substrate surfaces.¹⁹⁶

Similar to MOFs, COF-modified electrodes have also been frequently employed for electrochemical applications such as energy conversion,¹⁹⁵ energy storage,^{178,195} HER,¹⁹⁵ OER,¹⁹⁵ and eCO_2RR .¹⁹⁸ However, examples of COF-modified electrodes for the electrosynthesis of small organic compounds are scarce. Recently, Cai et al. reported a Ni(II)-modified COF film on fluorine-doped tin oxide (FTO) for the electrocatalytic oxidation of 5-hydroxymethylfurfural (HMF). To form the COF-modified WE, Ni(II) acetate was introduced to an organic scaffold consisting of trimethylphloroglucinol (Tp) and 5,5'-diamino-2,2'-bipyridine (Bpy). COF-modified WE was prepared via an interfacial crystallization method, “stamped” onto the FTO substrate, and finally soaked in nickel acetate solution to yield a nickel(II)-doped TpBpy-Ni film on FTO. The addition of nickel generates redox-active sites that allow for charge transfer by redox hopping. Electrolysis was carried out in 0.1 M $LiClO_4$ with an $E = 1.55$ V vs RHE. The resulting TpBpy-Ni@FTO electrode showed considerable electrocatalytic activity toward oxidation of HMF with conversion yield (58%) for FDCA. In comparison, it was shown that either bare FTO or TpBpy@FTO has no electrocatalytic response toward HMF oxidation (Scheme 5B).¹⁹⁹

Although these electrodes show promise in future applications, there are many limitations of their nature. For electrode modification with either MOF or COF, one needs to consider that deposition of the modifying layer onto the WE is mainly

limited to physisorption, causing great charge transfer resistance and lower electrode stability. Also, both materials are hard to synthesize and functionalize while exhibiting moderate to low electrical conductivity which further limits the wide application of this type of modification. Finally, morphology changes and active site poisoning greatly limit long-term applications of both materials.^{195,197,200,201}

6. ELECTRODE MODIFICATION OF SURFACE-CONFINED MEDIATORS

6.1. Surface-Confining Mediators

Surface-confined mediators are electroactive species anchored onto the surface of an electrode, enabling electron shuttling between the WE and species in solution. Two common categories of surface-confined redox species are surface-grafted mediators and self-assembled monolayers (SAMs). Surface-grafted mediators are molecular redox-active species immobilized on a substrate, typically through covalent bonding. Therefore, WE modification with surface-grafted mediators demonstrates strong redox reversibility and excellent chemical stability.^{202,203} In SAMs, individual molecules form an ordered ensemble on the surface of the substrate via chemisorption or physisorption that is established between the WE and the terminal group of the adsorbate. Modifying the WE with a molecular electrocatalyst features several advantages such as minimizing electrode fouling and eliminating the use of noble metals. Moreover, the chemical process for fixing molecular electrocatalyst, using either grafting or SAMs, is well-developed.^{204,205}

An important distinction must be made between mediators directly immobilized onto the surface of an electrode and those tethered with polymers, as discussed in Section 4.2.1. Both approaches can facilitate electroorganic synthesis through facile electron shuttling between the WE and the substrate in the solution. With surface-confined mediators, the general electrochemical behavior of the modified WE is close to that of free individual redox molecules; thus, the electrochemical response can be interpreted using the suit of conventional analytical and electroanalytical methodologies. However, in polymer-modified WEs the electrochemical response of the WE is very different from that of the individual redox molecule forming the polymer layer; thus, establishing the mechanism of the electrochemical reaction is more difficult.²⁰⁶ In comparison with surface-confined mediators (i.e., SAMs and surface-grafted mediators), preparation of a WE modified with polymer is more complex, as it requires additional steps to introduce a redox group or stabilize a polymeric film.¹⁴⁶ However, polymer-modified electrodes demonstrated stronger cycling stability when compared against examples using organic surface-confined mediators.²⁰⁷ Finally, surface-confined mediators feature higher

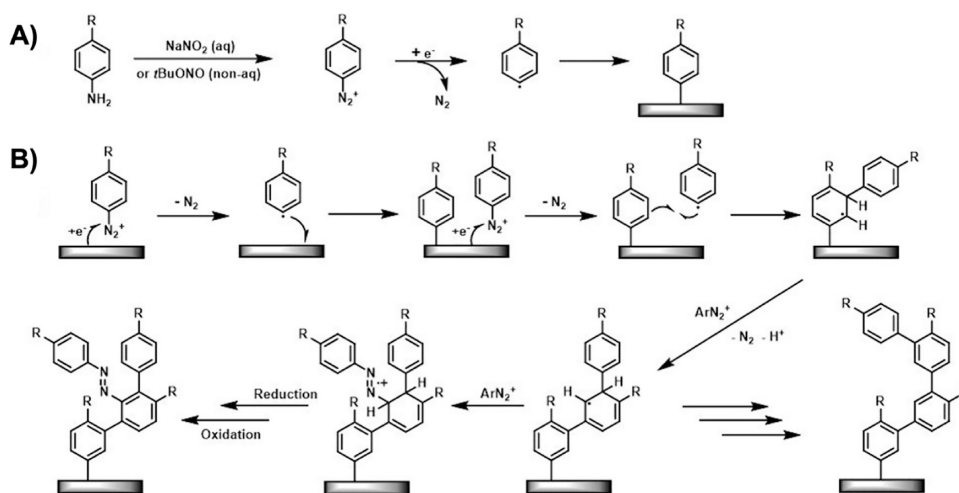


Figure 13. (A) Process of grafting organic molecules to a carbonaceous substrate and (B) formation of a multilayer structure onto the WE during a grafting reaction. Reprinted with permission from ref 214. Copyright 2021 American Chemical Society.

rates of heterogeneous electron transfer compared to polymer-modified WEs,²⁰⁸ while polymer modifications generally include a higher concentration of redox-active species per volume and, as a result, higher current density from the WE.²⁰⁹

Below, a brief description is provided for the modification of WEs with surface-grafted mediators and SAMs. Moreover, several relevant examples for the use of each modification approach toward organic electrochemistry are discussed.

6.2. Surface-Grafted Mediators and Applications toward Electroorganic Synthesis

Tethering via covalent bonding is the major approach for grafting a redox moiety to the WE. Establishment of the covalent bond leads to an irreversible graft, after which the immobilized molecule can only be removed from the surface under extreme redox potentials or extensive mechanical polishing. As a result, the modified electrode exhibits excellent chemical and electrochemical stability. Despite these unique advantages, surface-grafted mediators do possess certain limitations, as well. Namely, the mediator that is applied must be chosen with great care. Compared to its homogeneous form, there is limited space for mediator application, so an ideal candidate should exhibit a high turnover number and strong redox reversibility.²¹⁰ In addition, grafting may greatly alter the characteristics of the mediator, including selectivity, increasing the uncertainty associated with the choice of redox species.²¹⁰ Immobilization is also a more complex procedure than that of other electrode modifications, such as NPs, and is dependent on the functional groups of the mediator.

The specific method of grafting is a function of both the WE material and the anchoring group of the redox-active molecule. The simplified processes of grafting a molecular electrocatalyst to a carbon substrate are shown in Figure 13. In the majority of instances, grafting of a redox-active molecule onto a carbon substrate is accomplished by reductive cleavage of R–Y (Y = N₂, I, Br) to generate an aryl radical which can react with the sp² carbon center of the substrate and form a covalent bond (Figure 13A).^{211–213} The aryl radical can be generated either chemically or electrochemically.^{203,214,215} However, the nature of the radicals also allows for mediators to react with one another, making multilayer structures and forming dimerized product, thereby decreasing the efficiency of the grafting (Figure 13B).^{211,216–218}

Under certain conditions, this fabrication method has also been used to graft onto metal-based electrodes, such as Au.²¹⁹ The bonds with Au are weaker than those with carbon, making carbon-based electrodes a popular choice for surface-grafted modifications. Several functional groups such as amines, carboxylates, and diazonium salts are employed for grafting a redox molecule to the WE.²⁰³ Moreover, in recent years, methods such as physisorption were also identified to be successful grafting approaches. One example in which physisorption is used for the surface grafting of mediators is reported by Salehzadeh et al., wherein physisorbed 4-methylesculetin was employed for the electrooxidation of catechols.²²⁰ Common applications for surface-grafted mediators include sensors and biosensors,²²¹ the reduction of small molecules (NADH, H₂, CO₂, O₂),^{222–224} and water splitting.²²⁵

One major use of grafting in organic electrochemistry is to promote chemical and electrochemical stability of homogeneous redox mediators. For instance, the TEMPO mediator is a well-established catalyst for electrochemical C–H activation^{152,154,226} and electrooxidation of alcohols.^{202,227} However, as outlined in Section 4.2, TEMPO shows poor electrochemical stability once used as a homogeneous mediator. To resolve these issues, significant efforts were dedicated to modify a carbonaceous WE by grafting a TEMPO mediator.^{204,228–231} One outstanding example is the electrooxidation of various benzyl alcohol substrates using a CC WE modified with pyrene–TEMPO–MWCNT. As such, TEMPO was tethered to pyrene through amide coupling. Next, pyrene–TEMPO was immobilized onto the MWCNTs through π – π stacking interactions, forming a pyrene–TEMPO–MWCNT hybrid (Figure 14A). Finally, the CC WE was modified by pyrene–TEMPO–MWCNT through a dip-coating method using 0.02 wt % Nafion. CV studies showed that greater anodic current is produced using GC modified with TEMPO grafted to pyrene when compared to the use of homogeneous 4-acetamido-TEMPO (ACT) (Figure 14B–D). These results confirm higher electrocatalytic activity of the surface-grafted mediator. Further utility of the modified WE was confirmed through preparative electrolysis. Alcohol electrooxidation was carried out in an aqueous solution containing carbonate buffer at constant potential using an undivided three-electrode cell with CC-pyrene–TEMPO–MWCNT as the WE. Electrooxidation of benzyl alcohol using CC-pyrene–TEMPO–MWCNT affords

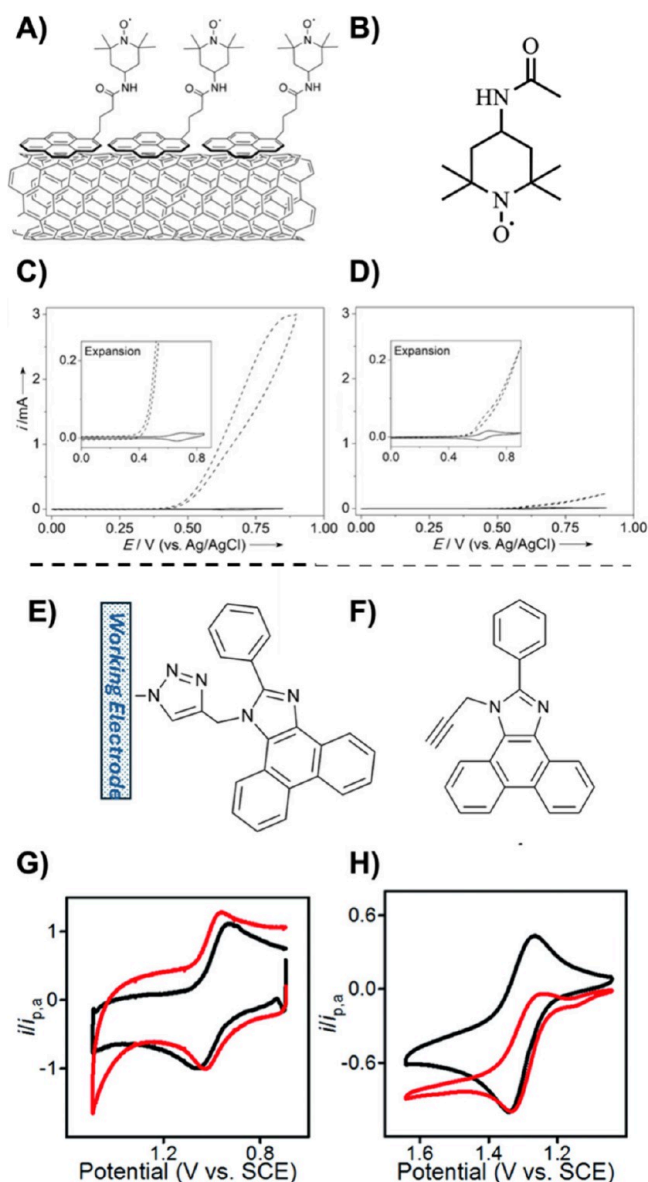


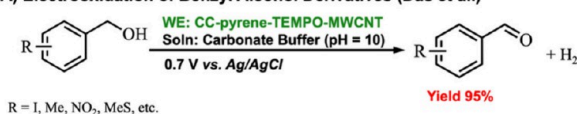
Figure 14. (A) and (C) Simplified scheme of Pyrene–TEMPO installation on MWCNT and corresponding CV studies, respectively. (B) and (D) molecular structure of ACT and relevant electrochemical studies. In panels (C) and (D) solid and dashed line represent CV studies in the absence and presence of benzyl alcohol substrate, respectively. Panels A, C, and D are reprinted with permission under a Creative Commons CC-BY 4.0 from ref 232. Copyright 2017 Wiley & Sons, Inc. (E) and (G) show structure of PIA derivatives grafted onto GC and corresponding CV studies, respectively. (F) and (H) display molecular structure of PIA derivative used as homogeneous redox mediator and the corresponding CV results, respectively. In panels G and H, black and red trace show CV results at 100 and 10 mV/s, respectively. Parts E, F, G, and H are reproduced under a Creative Commons CC-BY 3.0 from ref 237 with permission from the Royal Society of Chemistry.

full conversion within 50 min whereas use of 4-acetamido-TEMPO (ACT) as a homogeneous electrocatalyst yields negligible benzaldehyde, indicating the efficacy of electrocatalyst performance following grafting. Moreover, electrooxidation of 12 benzyl alcohol congeners using modified WE affords the corresponding aldehyde product in quantitative yield, which

further confirms broad utility of this type of WE modification for electrosynthetic purposes (Scheme 6A).²³²

Scheme 6. Reactions Schemes and Experimental Setup for (A) Electrooxidation of Substituted Benzyl Alcohols Using Pyrene–TEMPO-Modified CC Electrode and (B) Electrooxidation of an Alcohol and Ether Using PIA on GC

A) Electrooxidation of Benzyl Alcohol Derivatives (Das et al.)



B) Electrooxidation of Alcohol (Johnson et al.)



Besides TEMPO, several other mediators, such as aromatic amines²³³ and tetra(aminophenyl)porphyrin,²³⁴ were grafted to carbon substrate and employed for electroorganic reactions. A recent example is a report by Johnson et al., where the authors explored the electrooxidation of benzyl alcohol derivatives through the grafting of phenanthroimidazole (PIA) derivatives onto GC. PIA derivatives have shown to be an efficient family of homogeneous electrocatalysts for electrooxidation of alcohols.^{235,236} However, chemical stability of PIA derivatives is low, requiring a large quantity of the catalyst to carry out the electrooxidation process.²³⁷ To remediate this issue, PIA grafting onto GC was pursued through a cycloaddition reaction between a propargyl/propargyloxy group of the mediator and the already azide-modified GC, forming GC-PIA WE. The structure of the PIA congener grafted to the GC and one used as a homogeneous mediator is shown in Figure 14E and F, respectively. CV studies for GC modified with PIA GC show a totally reversible response at 10 and 100 mV/s, confirming stable electrochemical properties (Figure 14G). However, CV studies with a free PIA derivative show totally reversible behavior at 100 mV/s and a quasi-reversible response at 10 mV/s, indicating low electrochemical stability of free PIA (Figure 14H). Together with additional electrochemical studies, it was shown that anchoring PIA to GC significantly enhances electrochemical stability. Finally, increased electrochemical stability as a result of grafting was attributed to prevention of the dimerization of the oxidized PIA molecules.

Modified GC with PIA was employed for the electrooxidation of *p*-anisyl alcohol and 1-((benzyloxy)methyl)-4-methoxybenzene (Scheme 6B). Bulk electrolysis studies were conducted in a divided cell with ACN containing TBABF₄ as a supporting electrolyte and using GC modified with PIA derivatives as the WE. Compared against its homogeneous form, GC modified with PIA showed a 900- to 2300- and 1500-fold increase in turnover number for the electrooxidation of alcohols and ether, respectively. Besides increasing TOF, grafting PIA onto GC results in significant improvement in electrocatalytic functionality as is evidenced by the enhanced FE of 78% and conversion yield of 70%.²³⁷

6.3. Surface-Assembled Monolayers and Applications toward Electroorganic Synthesis

The individual subunits of SAMs are typically comprised of three parts including a headgroup, an anchoring group, and a long-chain backbone, connecting the anchoring and head groups. In SAMs, adhesion of individual subunits to the substrate is determined by the nature of the headgroup and substrate.²³⁸ The anchoring group in SAMs includes a range of organic motifs such as thiols, disulfides, amines, silanes, or carboxylic acids.^{239,240} Formation of SAMs is typically brought about by strong chemisorption between the substrate and headgroup.²⁴¹ Furthermore, strong inner-chain interactions (van der Waals) ensure tight packing and organization and further enhance the stability of monolayers.²⁴¹ Formation of the monolayer (tens of angstroms) allows for tremendous flexibility depending on the terminal functionality and chain length. Different combinations of ligands and head groups regulate surface properties such as wettability, surface accessibility, and selectivity of active sites.²⁴² A disadvantage of SAMs, however, is that installing bulky redox mediators will exhibit a great degree of disorder in the ultimate modification due to steric hindrance between adjacent subunits. Moreover, a WE modified with SAMs exhibits a limited potential window of stability.²⁴³ However, recent investigations by the Wuttig lab have shown that the limited potential window can be resolved via noncovalently anchored ammonium-based amphipathic molecules. This approach provided a stable potential window of 2.9 V, 0.9 V wider than previous covalent examples and 0.3 V wider than other noncovalent reports.²⁴³

Fabrication of SAMs is commonly achieved by chemisorption or physisorption onto an electrode. Chemisorption relies on the formation of covalent bonds between substrate and adsorbent, whereas physisorption preserves the electronic structure of the substrate with noncovalent electrostatic interactions. For electrochemical purposes, Au or other metals (Pt, Cu, and Ag) are the common electrode materials of choice. Au is particularly appealing because of its inert properties and established interactions with sulfur-based anchor groups (thiols, disulfides, and sulfides). One of most famous approaches for forming SAMs on Au substrate is using thiol-containing redox molecules. Immobilization of the redox mediator onto the Au substrate and formation of SAMs are shown in Figure 15A.²⁴⁴ In summary, the process involves chemical bonding of a molecule to an Au substrate through a thiol anchoring group, followed by chemical or electrochemical deprotonation of the thiol motif, forming a thiolate–Au bond. However, the nature of bonding between the SAM subunit and the substrate may vary between noncovalent and covalent depending on the pH of the solution. Moreover, the most successful SAM formation occurs with a dilute solution of precursor over the bare Au electrode. After initial immobilization, further modification is possible via covalent bonding with the terminal group.²⁴⁵

Generally, SAMs are employed for optical sensing,²⁴⁶ chemical sensing,²⁴¹ energy conversion, and small-molecule activation (e.g., OER and eCO₂RR). They are seldom utilized for electrosynthesis of small organic molecules; however, the following section discusses two examples highlighting the utility of SAMs for electrosynthetic purposes.

Electrogenerating radical intermediates via anodic decarboxylation has been widely employed for cross-coupling reactions and constructing different types of C–C motifs.^{11,247,248} However, decarboxylative cross-coupling suffers from several drawbacks such as requiring high oxidative potentials and low

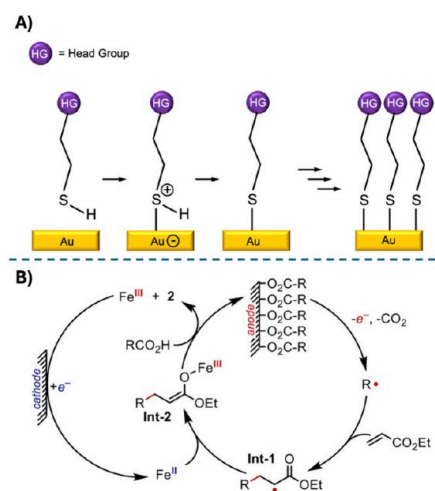


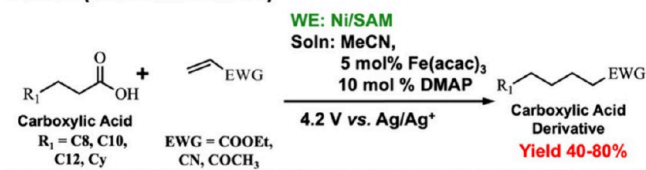
Figure 15. (A) Process of formation of SAMs on an Au substrate including chemisorption via thiol moiety, deprotonation, and accumulation to form an organized assembly and (B) the reaction mechanism for olefine arylation through a decarboxylative cross-coupling reaction. Panel B was reprinted under a Creative Commons CC-BY 4.0 from ref 250. Copyright 2022 Springer Nature.

efficiency due to the homocoupling reaction. Several approaches were developed to increase efficiency and yield of anodic decarboxylation.^{11,249} One of these methods is self-assembly of carboxylic derivatives onto metal WEs. Hintz et al. employed this methodology for decarboxylative alkylation of various olefins. Electrochemical transformation is carried out in ACN containing 4-(dimethylamino)pyridine, Fe(acac)₃, and with decanoic acid and ethyl acrylate as starting reagents using Ni foam as the WE and RVC as the counter electrode. Optimization studies together with several types of electrochemical measurements revealed the reaction mechanism to include steps shown in Figure 15B. In this reaction, deprotonated decanoic acid adsorbs onto Ni and forms an ordered structure of the SAM. Upon one-electron oxidation, electrogenerated aryl radical releases into solution, where it immediately reacts with ethyl acrylate to form intermediate 1 (i.e., **Int-1** in Figure 15B). Once formed, **Int-1** couples with Fe(II), which is generated at the cathode, forming intermediate 2 (i.e., **Int-2** in Figure 15B). Finally, **Int-2** reacts homogeneously with 1 equiv of protonated decanoic acid, forming alkylate product, and 1 equiv of deprotonated carboxylic acid and regenerating Fe(III). This decarboxylative cross-coupling is shown to be effective on eight aliphatic carboxylic acid derivatives with yields ranging from 40% to 80% (Scheme 7A). Formation and continuous regeneration of SAMs is key for efficient decarboxylative cross-coupling by (i) enhancing electrochemical performance through minimizing undesirable passivation as well as oxidative leaching of Ni and (ii) minimizing undesired oxidation of alkyl radical and acrylate thereby decreasing extended of side reactions such as homocoupling.²⁵⁰

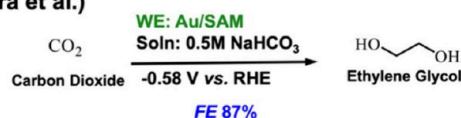
Another example of using SAMs is to minimize HER for electrochemical reactions that occur at deeply reductive potentials, thereby promoting product selectivity. Heavy metals such as Hg and Pb have been shown to be an effective solution to minimize HER under deeply reductive conditions. However, use of these metals is limited due to environmental and health-related concerns. An example is a report by Tamura et al. where 1-methylimidazolium-terminated SAMs on Au were employed for selective and efficient electroreduction of CO₂ to ethylene

Scheme 7. Reaction Scheme and Experimental Setup for (A) Catalyst-Controlled Electrooxidation of Carboxylic Acids Using a SAM-Modified Ni Foam Electrode and (B) Electroreduction of CO₂ to Ethylene Glycol Using a SAM-Modified Au Electrode

A) Catalyst-controlled Electrooxidation of Carboxylic Acids (Hintz and Sevov)



B) Electroreduction of CO₂ to Ethylene Glycol (Tamura et al.)



glycol while suppressing HER. Modified WE was prepared by soaking a pristine piece of Au in an ethanolic solution of thiol-terminated 1-methylimidazolium salt for 24 h. Electrochemical CO₂ reduction was carried out in 0.5 M NaHCO₃ aqueous solution saturated with CO₂ using a two-compartment electrochemical cell and an Au-modified WE. It was shown that the electrochemical reduction of CO₂ yields ethylene glycol at high FE (87%) while minimizing CO evolution. In contrast, reduction of CO₂ at a bare Au electrode only produces CO with low FE (26%), while requiring a large overpotential (Scheme 7B).²⁵¹

Finally, one needs to consider a few drawbacks when modifying the WE through either grafting or self-assembled monolayers (SAMs). Grafting is a low-efficiency process and often results in sporadic coverage of the WE surface. Additionally, grafting involves a multistep organic or electrochemical reaction that is complicated and has limited options for substrates and redox molecules. Similarly, SAMs are also limited

in terms of substrate choice. Furthermore, SAM is not an ideal strategy for modifying WE surfaces with large redox mediators or porous substrate.

7. CONCLUSION

As mentioned earlier, the choice of electrode material for all electrochemical studies heavily depends on the redox reaction of interest and the desired outcomes. This is particularly crucial in organic electrosynthesis, where selectivity, specificity, and yield are paramount. Altering the composition of the WE can significantly influence the product distribution and yield in electroorganic reactions. Therefore, meticulous selection of the WE and precise engineering of the WE–solvent interface are essential to control the outcome of the electrosynthetic reaction. Each material discussed in the preceding sections possesses distinct electrochemical properties, along with its own set of advantages and disadvantages (Table 1). This Review aims to provide a solid starting point for selecting the electrode composition that best achieves desired reaction outcomes. Moreover, this highlights the vast possibilities for developing new WE materials tailored for targeted electroorganic reactions. Given that electroorganic synthesis and materials science are rapidly evolving research fields, there are exciting opportunities to explore novel electrode compositions to maximize the reaction yield and selectivity while decreasing the applied electrochemical potential. Several interesting candidates include NPs, MOFs, and semiconductor composite materials. These materials, though employed frequently in other electrochemical applications, have untapped potential as WE materials for advancing organic electrochemical transformations and developing new electroorganic schemes.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article.

Table 1. Advantages and Disadvantages of Each Discussed Electrode Modification for Electroorganic Synthesis

electrode modification	advantages	disadvantages
nanoparticles	high surface area improved electrocatalytic properties enhanced control over microenvironment low cost of preparation	possible loss of electrochemical activity due to deactivation and detachment for large-scale applications or extended electrolysis
composite material	introducing unique electrocatalytic properties highly modifiable electrochemical stability	poor reproducibility (i.e., NP agglomeration) complex fabrication difficult to analyze detailed mechanism of reaction due to electrode low conductivity and limited area of the WE
polymers	highly tunable highly conductive introduce novel features (e.g., anti-fouling)	poor reproducibility poor adhesion decay of electrochemical performance and conductivity
organic frameworks	large surface area structural flexibility and tunability high chemical stability	low conductivity low adhesion to WE
surface-confined mediators	excellent chemical and electrochemical stability for surface-grafted mediators easy modification easy to analyze reaction mechanism	low surface concentration surface area grafting may alter electrochemical characteristics substrate limitations disorder via steric hindrance small potential window of stability for SAMs

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Author Contributions

A.C.R.: investigation, writing—original draft, and editing; K.E.P.: investigation, writing—original draft, and preparing reaction schemes; C.T.L.: investigation, writing—original draft, editing, and preparing figures and reaction schemes; S.A.S.: investigation, writing—original draft, editing, and preparing figures and reaction schemes; S.H.: conceptualization, supervision, and writing—review and editing.

Notes

The authors declare no competing financial interest.

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