

Immobilization of Discrete Electrocatalysts on Carbon Surfaces

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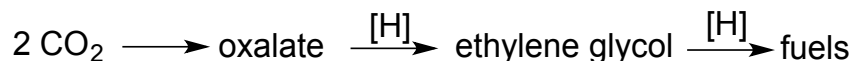
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Abstract:

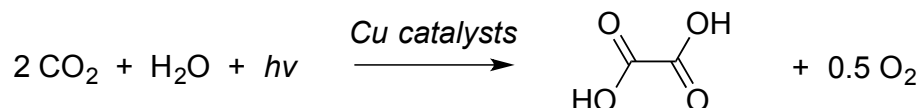
Our research focus has been on the development of discrete metal catalysts on carbon surfaces to achieve electrocatalytic oxidation of fuels such as methanol or reduction of CO₂ or O₂ to oxalate or water, respectively. Developing reproducible synthetic coupling strategies of discrete metal complexes to carbon surfaces is one step toward realizing electrocatalytic conversion; a more robust and reproducible chemical attachment strategy to high surface carbon materials has been developed using an synthetic pathway that includes postderivatization robust “click” attachment. Three distinct areas have been investigated. (1) Click attachment of discrete ruthenium complexes that show electrocatalytic oxidation of methanol to formaldehyde, but the active species is now best understood as ruthenium metal sequestered on the carbon electrode. (2) Discrete copper catalysts immobilized on carbon electrocatalytically do not couple CO₂ to oxalate as reported in the literature, though our DFT calculations suggest only modest CO₂ coupling barriers using simple macrocyclic amine copper complexes. (3) A 10-fold enhanced reduction reactivity of O₂ to water from an imprinting dimeric copper catalyst as compared to its randomly distributed monomeric counterpart highlights a new synthetic strategy for creating multinuclear metal catalyst sites for surface-immobilized electrocatalysis.

Introduction:

The production of carbon-based fuels and chemicals from both renewable energy and materials is of utmost importance for a sustainable and energy-efficient society. The emerging technologies that directly convert sunlight to energy serve as an important starting point in creating a renewable energy economy, but the intermittent and diffuse availability of sunlight requires that the harvested energy be transformed to high energy density and storable fuels. Developing energy-efficient processes that reductively couple CO₂, an abundant and renewable C₁ source, for the production of value-added chemicals with electrons derived from water oxidation is a goal of great importance. Currently, less than 1% of anthropogenic CO₂ is used for the production of chemicals. A game-changing strategy would be the synthesis of higher order C_n (n > 1) products and fuels from CO₂, but this practice is limited due to the extreme challenges associated with C-C bond formation and water oxidation under energy-efficient conditions. Developing catalysts capable of efficiently coupling CO₂ to oxalate and subsequently to other C₂ compounds would provide a novel strategy to make value-added chemicals not dependent on fossil fuel reserves.



A long-term vision is the capture and conversion of CO₂ from gas- or coal-fired power plants to large-scale, value-added chemicals or fuels with electrons derived from solar-powered water oxidation. The overall transformation resembles photosynthesis, in which nature uses solar power to drive the conversion of CO₂ and water to C_n chemicals and O₂.



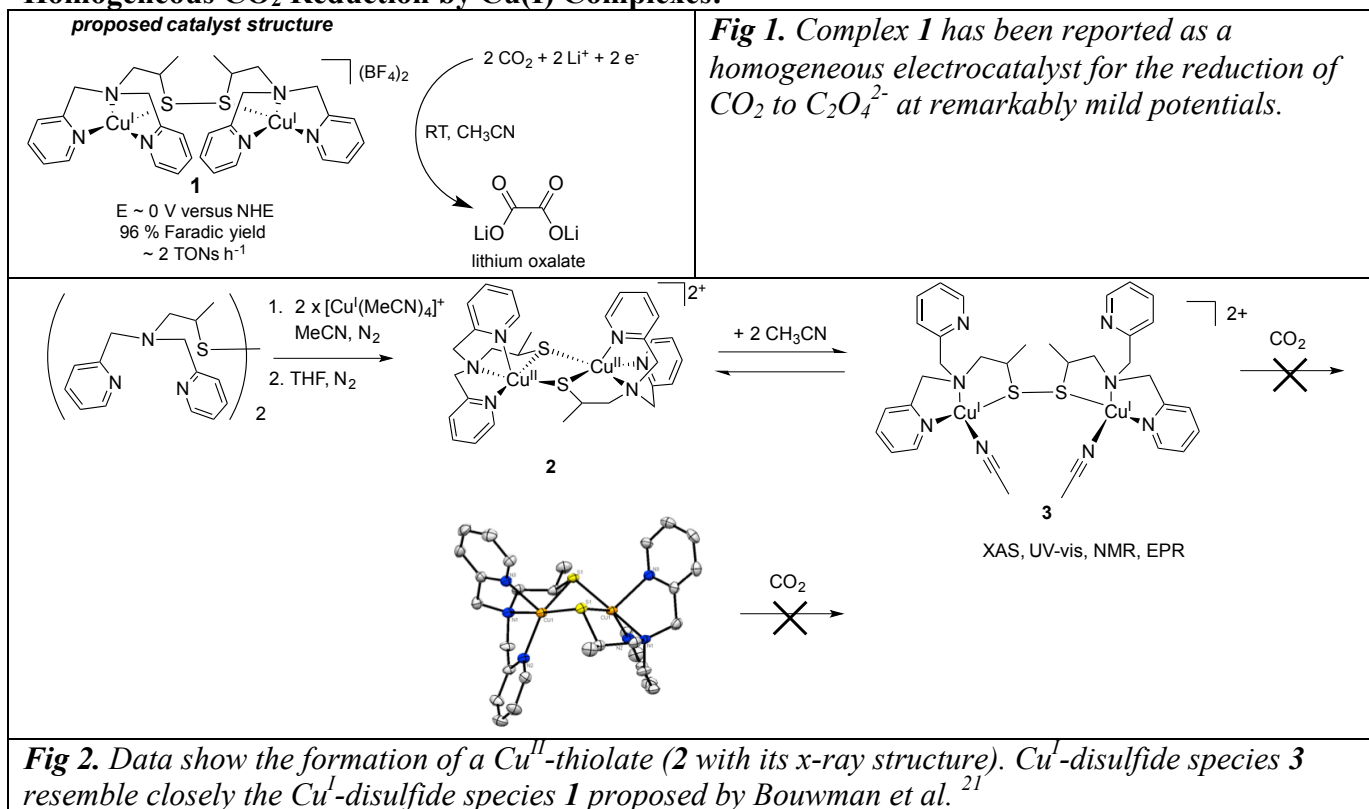
Developing kinetically rapid, durable catalysts for new transformations is one of our research major goals. Molecular catalysts have been particularly important in this endeavor because of their synthetic variability, which provides structure-reactivity information. Immobilizing molecular catalysts on electroactive heterogeneous scaffolds makes catalyst separation from products facile, and is an alternative to catalysis with noble metal surfaces.

A variety of methods exist for covalent attachment of molecular species to heterogeneous surfaces. Molecular complexes have been immobilized covalently on numerous surfaces (carbon,^{1,2,3} metal,⁴ metal oxide,^{5,6} silicon,⁷ and metal organic frameworks⁸) via a variety of techniques (copper catalyzed azide-alkyne cycloaddition,^{3,9} silane deposition,¹⁰ electrochemical grafting,¹ thiol-Au binding,⁴ phosphonate¹¹ and carboxylate¹² binding). Covalently attached, surface-immobilized molecular complexes have demonstrated water oxidation,^{13,14} carbon dioxide reduction,^{15,16} and alcohol oxidation,^{5,17,18} reactions, which is related to their homogeneous catalyst counterparts.^{14,19} The potential advantage of immobilized variants is the elimination of deactivation pathways possible or probable with solution species, thereby highlighting new active species of interest.²⁰

Our ongoing research focuses on the development of metal-based catalysts attached to inexpensive carbon electrodes for electrocatalytic oxidative or reductive processes. The proposed research entails ligand synthesis, homogeneous catalyst screening, catalyst immobilization on carbon surfaces, and mechanistic analysis, along with complementary density functional theory (DFT) calculations to probe potential reaction mechanisms. Significant effort is directed into the systematic derivatization of carbon surfaces to assure reproducible attachment strategies.

Results:

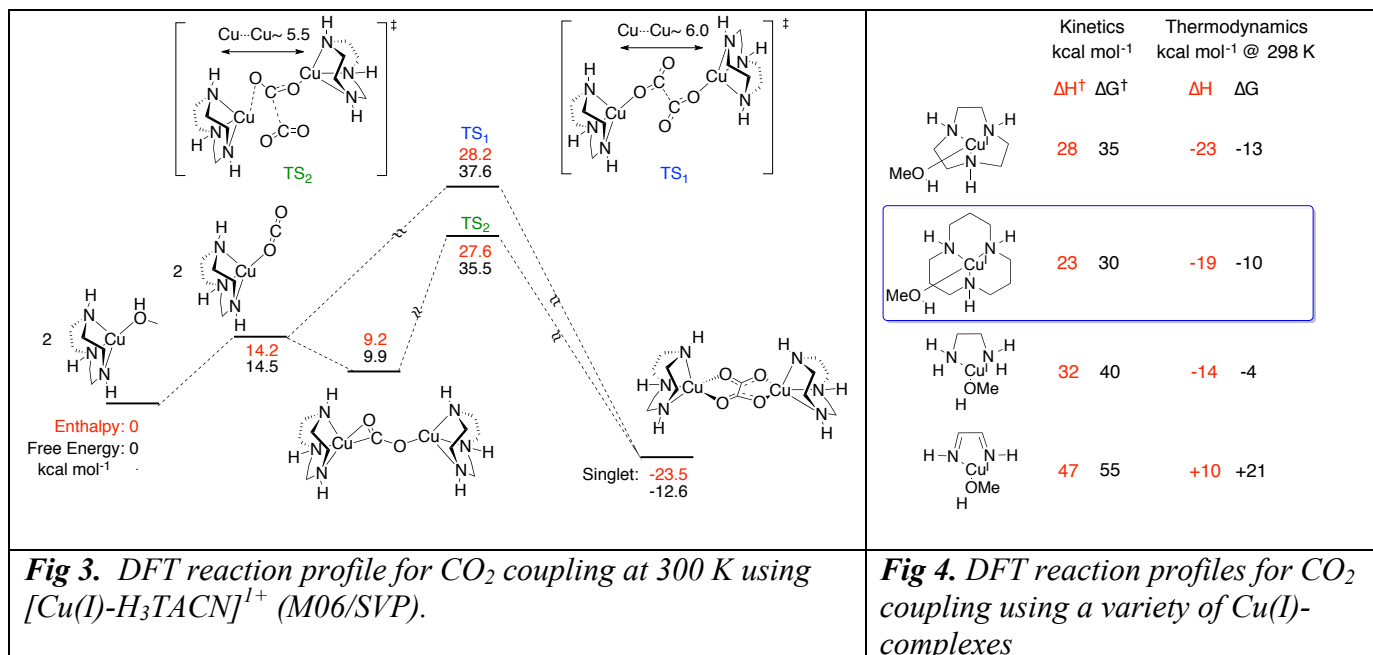
Homogeneous CO₂ Reduction by Cu(I) Complexes:



We have investigated the reductive coupling of CO₂ to oxalate by simple copper complexes. The addition of [Cu^I(MeCN)₄]BF₄ to the disulfide ligand is reported in the literature to yield a μ-disulfido Cu(I)Cu(I) complex (**1**) capable of stoichiometrically and electrocatalytically coupling CO₂ to oxalate (**Fig 1**) at remarkably mild potentials.²¹

In our hands, the solid state x-ray structure shows that the disulfide bond is reduced upon the copper coordination to give a μ-thiolato Cu(II)Cu(II) dimeric structure (**2**). Spectroscopic evidence (X-ray Absorption Spectroscopy, UV-vis spectroscopy, NMR) suggest that a μ-disulfido Cu(I)Cu(I) species (**3**) is in equilibrium with **2** in an acetonitrile solution (**Fig 2**), yet we have found no evidence of stoichiometric or electrocatalytic CO₂ reductive coupling to oxalate with this complex.²¹ A paper detailing redox behavior of the ligand has been published.²²

DFT calculations suggest that the coupling free energy barriers of CO₂ to oxalate with Cu(I)-aza macrocyclic complexes are reasonable, as low as 30 kcal mol⁻¹ (**Fig 4**). Such barriers would lead to very slow reaction rates under ambient conditions, but higher temperatures might be viable (**Fig 3 & 4**). The potential energy surfaces of an entire family of Cu(I)-aza macrocyclic complexes were calculated to determine the lowest coupling barrier. In each case, an asymmetric transition state is correlated with the lowest free energy barrier. The Cu(I) complexes with the lowest barriers possess the attribute that their Cu(I) forms are highly stabilized and the steric demands of the ligand are minimized. In all cases, the reaction is calculated to be exergonic. With this information, we screened a variety of Cu(I) aza-macrocycles for CO₂ coupling both at ambient and elevated temperature, but under no conditions could we detect oxalate formation.



Two other Cu complexes with nitrogen-based ligands are reported in the literature to promote stoichiometric formation of oxalate products under remarkably mild conditions (**Fig 5**).^{23,24} By literature precedent, the CO₂ reaction of the Cu(I) complexes with the more electron-donating triazacyclononane (TACN) ligand (**L**₁) is faster than that with the aromatic nitrogen ligand (**L**₂), but in both cases the

oxalate yield is low and characterization has relied solely on x-ray crystallography. As above, we have explored the coupling capacity of these two complexes with CO_2 ,²³ and do not find any significant oxalate formation under all conditions attempted. We must conclude from our investigations that coupling of CO_2 using cationic aza-macrocylic Cu(I) complexes is not a viable strategy to oxalate formation at temperatures below 100°C .

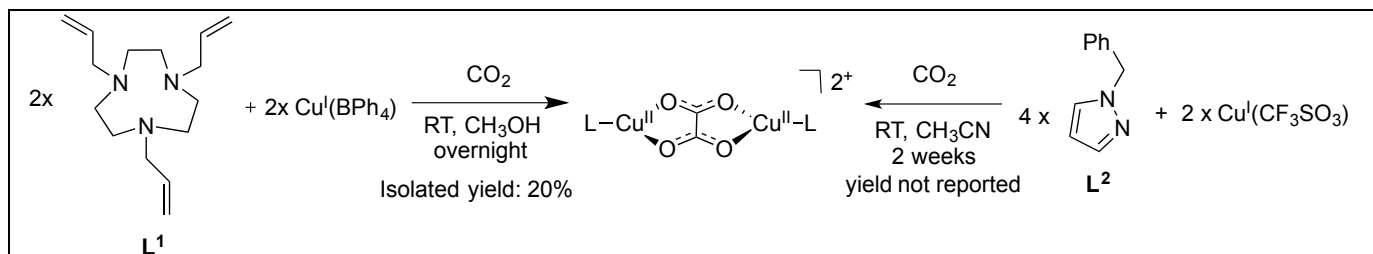


Fig 5. Literature examples of Cu^{I} -mediated reductive coupling of CO_2 to oxalate.^{23,24}

Immobilized Discrete Copper Electrocatalysts for O_2 Reduction: Cu catalysts



Water oxidation and dioxygen reduction are microscopic reverse processes (eqn 1) that share common reaction mechanisms. The ability of discrete copper complexes to catalyze the electro-oxidation/reduction of water/dioxygen is well documented.²⁵⁻²⁷ Studies of dioxygen reduction inform on the design of electrocatalysts for efficient water oxidation. Using a methodology developed in our labs, Cu(1,10-phenanthroline) complexes have been attached covalently to glassy carbon electrodes (GCE). The ability to reduce O_2 efficiently is related to the number of dinuclear copper sites on the electrode.²⁵ Meyer *et al.* have demonstrated recently that the electrocatalytic rate of water oxidation by copper catalysts have a second-order rate dependence on the copper catalyst.²⁷ Although our previous work has focused on O_2 reduction, the principles for creating dinuclear species should be applicable to water oxidation (**Fig 6**).

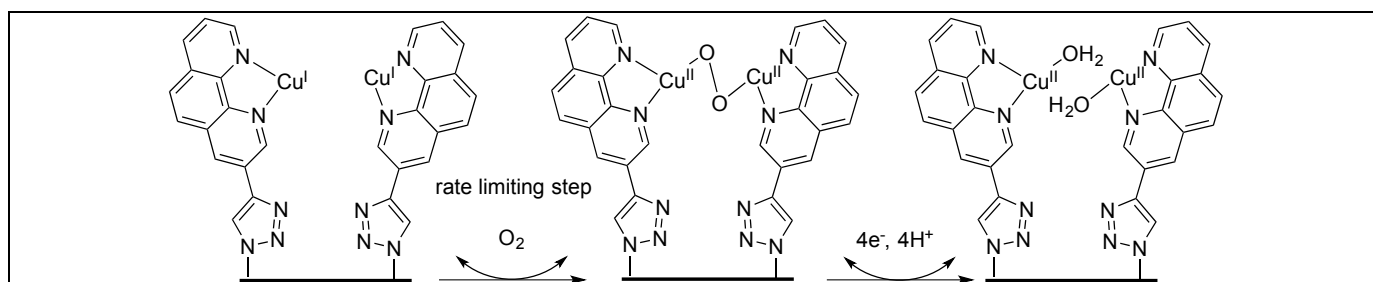
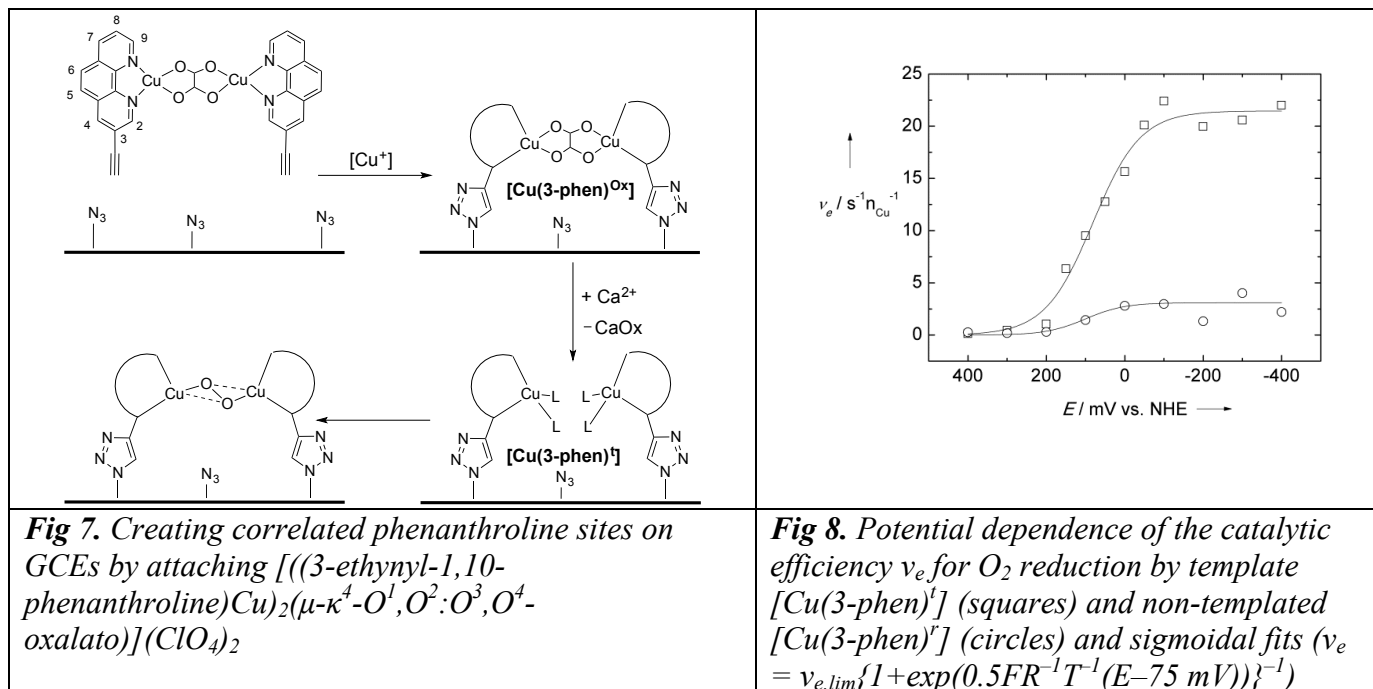


Fig 6. Schematic illustrations of dioxygen reduction and water oxidation, two microscopic reversible steps, catalyzed by immobilized dinuclear copper complexes.

The catalysts are immobilized through a 1,3-dipolar azide-alkyne cycloaddition between a ligand with an ethynyl group and an azide moiety on the GCE surface.²⁸ Polynuclear ligand binding sites can be created effectively on a GCE by two methods: (a) controlled azide surface density or (b) templating dinuclear sites by immobilization of complexes with a removable bridge, an imprinting technique. The oxalate anion has been used successfully to imprint dinuclear Cu phenanthroline sites (**Fig 7**), even under surface-diluted conditions. A comparison of the kinetic current from O_2 reduction versus copper

catalyst surface coverage of both randomly distributed Cu-phenanthroline complexes and imprinted dimeric sites shows significantly more current (~10-fold increase) with the latter exhibiting a greater faradaic efficiency to water (**Fig 8**), highlighting the importance of a correlated arrangement of the metal centers on the electrode surface for fast and energy efficient conversions.



Hydrosilylation of CO_2 – Reductive Coupling to Formic Acid and New Silicone Materials

In the process of investigating CO_2 coupling with discrete copper complexes, we have discovered a facile, quantitative hydrosilylation of CO_2 by polyhydrosiloxane to prepare formoxylated polysiloxane. The resulting formoxylated polysiloxane releases formic acid when treated with water or an alcohol, completing the CO_2 to fuel objective, but more importantly, this material crosslinks readily to an elastomeric silicone that exhibits thermal self-healing behavior even in the presence of water (**Fig 9**). A highly efficient Cu(I) hydride catalyst is a key enabling step to these new smart materials from two by-products, polyhydrosiloxane and CO_2 .

This study details a new strategy for the reductive integration of CO_2 into a polymeric elastomer with healing properties that is tolerant of wet conditions. Efficient CO_2 hydrosilylation using an earth-abundant metal catalyst (copper) allows for the simple preparation of formoxylated polysiloxane (PFMS) from two abundant industrial by-products in 1 hour. Engineering of latent reactive groups that generate healing components *in situ* upon damages provides a new approach for future polymer-healing designs. Further exploration of PFMS as a crosslinking component in silicone rubbers may provide greener alternatives to commercial acetoxy silanes, in which the carbons are derived exclusively from fossil fuels. The remarkably high mass ratio of CO_2 in the PFMS (*ca.* 40%) and in the formed elastomers (*ca.* 4-10%) unequivocally demonstrates the great potential of CO_2 as a useful carbon source to make polymers via a reductive approach.

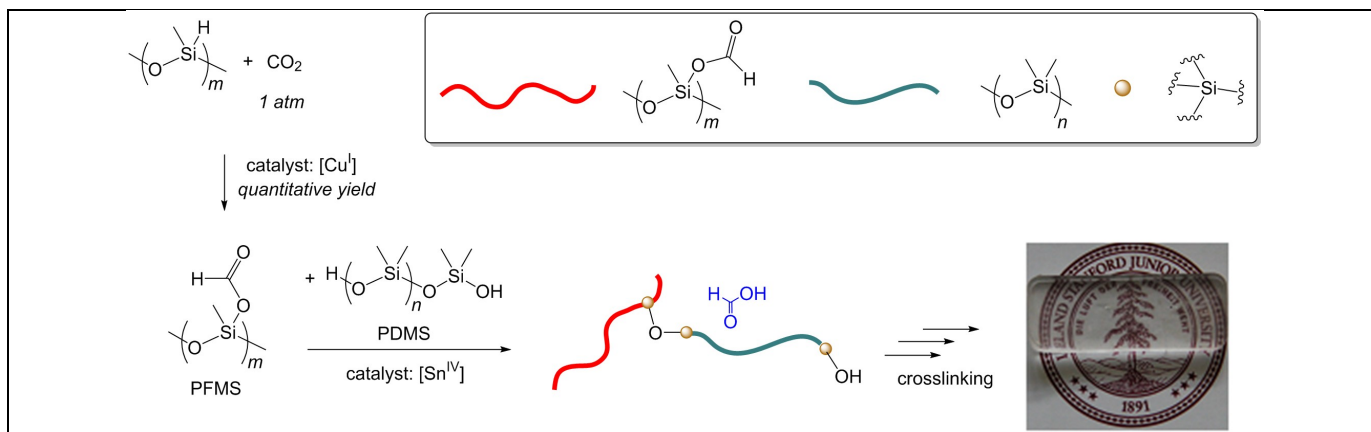


Fig 9. Water-activated healable silicone rubbers derived for CO₂ and polymethylhydrosiloxane elastomers.

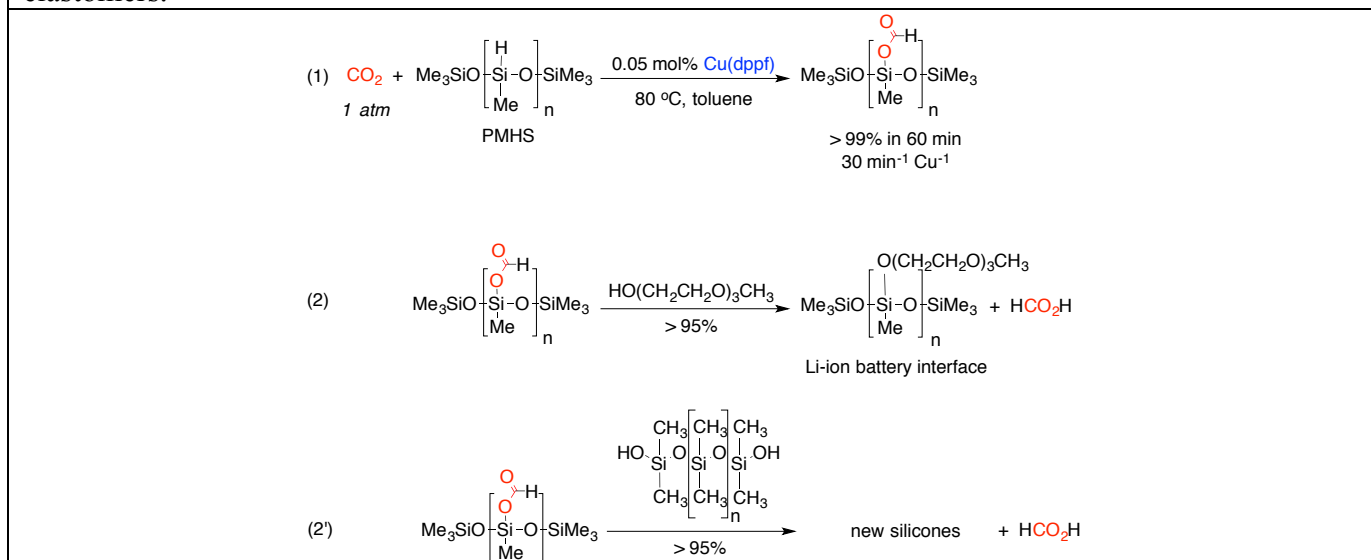


Fig 10. Water-activated healable silicone rubbers derived for CO₂ and polymethylhydrosiloxane elastomers.

Development of Robust and Reproducible Attachment Points on High-Surface Area Carbons

Developing efficient and reproducible covalent surface functionalization methods for high surface area, porous carbon materials is an area of considerable research interest due to their low cost. Surface modification allows for tuning the chemical and physical properties of these materials increasing the range of their applications, including energy storage and gas separations. Ideally, introduced functionality is robust and provides a versatile attachment point for further chemical modification. Current carbon surface functionalization strategies such as radical coupling of amines, coupling of alkynes at high temperatures, and photochemical coupling of alkynes are limited in scope, relatively unselective, and often require aggressive reaction conditions.

Chloromethylation of high-surface carbons is possible with good coverage of *ca.* 1.5 mmol g⁻¹, yet the hazardous procedure is difficult to perform and yields an electrophile for nucleophilic displacement that is far from ideal if high derivatization yields are desired.²⁹ We have developed and optimized simple, safe and reproducible bromomethylation of high-surface area carbons. The bromomethylated materials

(**Br-AC**) have high surface coverage (*ca.* 1.2 mmol g⁻¹), exhibit excellent stability (100 days, < 5 % Br loss), and react readily with a variety of nucleophiles in high yields. Derivatization with azide is a particularly attractive material (**N₃-AC**) for further derivatization using Cu(I) catalyzed azide-alkyne cycloaddition reaction (CuAAC). **N₃-AC** also displays excellent stability and can be coupled with various terminal alkynes to yield functional materials, as detailed below.

Treatment of **Br-AC** with sodium azide in DMSO affords **N₃-AC** with typically greater than 90% conversion of Br to N₃, as determined by nitrogen elemental analysis, and in agreement with XRF data for **N₃-AC** showing only 4 – 8% of the initial Br content remaining after the reaction. The Br 3d and N 1s regions of the XPS spectrum of **N₃-AC** confirm the high conversion of Br to N₃. The intensity of the two diagnostic N 1s XPS features of azide (401 & 405 eV) deviate from the expected 1:2 ratio significantly (*ca.* 1:4), suggesting partial azide decomposition to yield amine-like nitrogen species on the surface. In addition to functionalization of **Br-AC** by simple nucleophilic displacement, CuAAC has been performed on **N₃-AC** with various ethynylated substrates. Ethynyl-ferrocene was first chosen as a model substrate to provide an elemental tag (Fe) for characterization by XRF and XPS. CuAAC of ethynyl ferrocene on **N₃-AC** resulted in ferrocene-functionalized materials (**Fc-AC**) with Fe loadings of up to 1.0 mmol g⁻¹ as measured by XRF, corresponding to approximately 90% conversion of azide from **N₃-AC**. The N 1s region of the XPS spectrum of **Fc-AC** displays a single peak near 401 eV, suggesting good conversion of azide to triazole during the CuAAC reaction. The Fe 2p_{3/2} region shows distinct features associated with Fe(II), confirming incorporation of Fe onto the surface of AC.

Additional functionalization of **N₃-AC** using various ethynylated amines was explored as a first step toward creating discrete molecular functionalized carbon materials, including ones that should be capable of metal chelation. Most notably CuAAC of ethynyl ethylenediamine and ethynyl propylenediamine on **N₃-AC** gave diamine-functionalized materials **cED-AC** and **cPD-AC**, respectively. The N 1s region of the XPS spectrum of **cED-AC** and **cPD-AC** suggests near complete conversion of the azide functionality to triazoles, and nitrogen elemental analysis confirms an efficient conversion. Surface loadings of *ca.* 1.0 mmol g⁻¹ of diamines are achieved from **Br-AC** materials containing *ca.* 1.2 mmol g⁻¹ of bromide.

We also explored additional functionalization of **Br-AC** using simple nucleophilic bromide displacement by diamines. Mixing previously characterized **Br-AC** with neat ethylenediamine or propylenediamine yields another set of diamine-functionalized materials (**ED-AC** and **PD-AC**, respectively). XRF of these materials show a 90% decrease in bromine content and elemental analysis confirms a diamine concentration of *ca.* 1.1 mmol g⁻¹ for both the **ED-AC** and **PD-AC** materials.

A Discrete, Surface-immobilized Ruthenium Electrocatalyst for Alcohol Oxidation

A discrete ruthenium polypyridyl complex has been immobilized on carbon via CuAAC, along with other metal oxide surfaces. From this precursor an electrochemically generated ruthenium species is formed that oxidizes benzyl alcohol with a modest overpotential and methanol oxidation that would be the first example of a discrete metal species immobilized to an electroactive surface capable of this difficult transformation. It is now clear, that the electrocatalysis does not arise from the discrete species, but is better understood as ruthenium metal deposited onto the carbon electrode.

The [RuCl(DMSO)(ethynyl-TPA)]PF₆ (TPA-Ru) complex was attached covalently to azide-functionalized carbon (GC-TPA-Ru) in addition to ITO and FTO by a similar immobilization strategy.

The carbon was prepared according to a previously reported procedure.³⁰ Cyclic voltammetry (CV) was used to characterize GC-TPA-Ru. A reversible redox couple is observed at 1.15 V vs NHE (all potentials reported vs NHE), and is assigned to the Ru^{II/III} couple of the [RuCl(DMSO)(ethynyl-TPA)]⁺ complex on the surface. The peak current shows a linear dependence on scan rate, corroborating surface immobilization of the complex. Integration of the area of the cathodic wave at 1.15 V corresponds to an average surface coverage of 3×10^{14} redox active Ru molecules cm⁻².¹¹ A quasi-reversible reduction wave is observed at 0.60 V that does not appear unless the oxidation sweep of the potential passes the Ru^{II/III} couple. The 0.60 V reduction wave has been assigned previously to the reduction of Ru^{III}-DMSO, whereas the reduction at 1.15 V is Ru^{III}-DMSO.^{31,32}

Ethynyl-TPA-Ru is a derivative of [RuCl(DMSO)(TPA)]PF₆ that can be immobilized on azide functionalized surfaces through CuAAC. The redox potential of the ethynyl-TPA-Ru complex agrees with that reported in the literature for the non-ethynyl compound, RuCl(DMSO)(TPA)]PF₆,^{10,12,13} suggesting that the ethynyl group does not significantly alter the potential of the Ru^{III/II} redox couple of this complex in solution. Further, the same redox couple for ethynyl-TPA-Ru in solution and GC-TPA-Ru, ITO-TPA-Ru, and FTO-TPA-Ru surfaces suggests that ethynyl-TPA-Ru is immobilized as a discrete molecular complex on each electrode surface and the electrode surface does not significantly change the redox potential of the discrete complex observed in homogeneous solutions. The linear correlation of peak current with scan rate for GC-TPA-Ru corroborates a surface immobilized redox couple. This demonstrates that discrete molecules coupled to surfaces retain their intrinsic reduction potential on such surfaces.

Methanol oxidation is observed from GC-TPA-Ru but not from ITO-TPA-Ru or FTO-TPA-Ru, which suggests there is a unique property associated with the glassy carbon surface to enable methanol oxidation. Alcohol oxidation under aqueous conditions suggests that a Ru-oxo species may be an intermediate in catalysis. Alcohol oxidation from GC-polish-soak-Ru and GC-N₃-soak-Ru at the same onset potential as GC-TPA-Ru suggests that the TPA-Ru complex is not the active catalyst involved in alcohol oxidation. These results do suggest that RuCl₂(DMSO)₄ is a precursor to an active alcohol oxidation catalyst. Evidence in the literature suggests that ruthenium nanoparticles may form from ruthenium (II) dichloride salts in refluxing alcohol solutions, and carbon serves to limit particle agglomeration.¹⁴ Similar onset potentials between the covalently immobilized GC-TPA-Ru and the GC-polish-soak-Ru suggest that the methanol oxidation is not arising from TPA-Ru covalently immobilized on the electrode, but adventitious ruthenium on the glassy carbon. The lack of methanol oxidation from metal oxide electrode surfaces suggests that the adventitious ruthenium does not adsorb to the metal oxides. This evidence suggests that rather than a discrete covalently immobilized ruthenium electrocatalyst, adventitious ruthenium is responsible for the observed methanol oxidation. Discrete ethynyl-TPA-Ru is immobilized on each electrode surface via CuAAC, but adventitious Ru preferentially binds to glassy carbon.

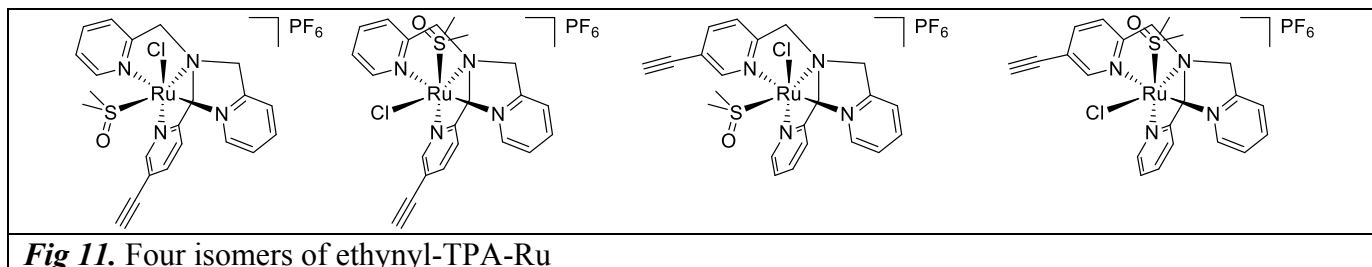


Table 1. $E_{1/2}$ for Ru^{III/II} couple in solution and on surfaces.

	pH 1 HClO ₄	0.1 M [NBu ₄]PF ₆ MeCN
	E V vs. NHE	E V vs. Fc ^{0/+}
trans-TPA-Ru ^{a,b}	N/A	0.62
cis-TPA-Ru ^{a,b}	N/A	0.58
Ethynyl-TPA-Ru ^b	1.15	0.61
GC-TPA-Ru ^c	1.15	0.65
ITO-TPA-Ru ^c	1.14	0.69
FTO-TPA-Ru ^c	1.16	-

^aRef 13, ^bHomogeneous, ^cSurface Immobilized

Table 2. Onset Potential for Alcohol Oxidation

Ruthenium Complex	pH 1		pH 5	
	Benzyl Alcohol ^c	Methanol ^d	Benzyl Alcohol ^c	Methanol ^d
cis-RuCl ₂ (DMSO) ₄ ^a	0.87	1.28/0.96	1.11/0.61	0.98/0.64
[RuCl(DMSO)(TPA)]PF ₆ ^{a,e}	1.16	-	0.79	Not Observed
[RuCl(DMSO)(ethynyl-TPA)]PF ₆ ^a	0.97	-	0.61	0.72
GC-TPA-Ru ^b	1.0	0.97	0.62	0.76
GC-polished-soak-Ru ^b	0.86	-	0.58	0.7
GC-N ₃ -soak-Ru ^b	0.90	-	0.59	0.70
ITO-TPA-Ru ^b	0.93	-	0.80	-
FTO-TPA-Ru ^b	0.98	-	-	-

^aHomogeneous complex in solution. ^bSurface Complex. ^c 6mM. ^d 100mM. ^e mixture of isomers.

Future Plans:

In the last months of this grant, we will continue to focus on those aspects of the research that will be most impactful to future energy related research, namely the imprinting of molecular catalysts on carbon electrodes and derivatization of high-surface area carbon materials.

Budget:

The current budget is projected to be spent out by the middle of the summer 2017. 1 graduate student is now working on carbon electrode modification/electrocatalysis and high-surface area carbon modifications.

Scope of Project:

The scope of the project has not changed.

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