Final Project Report

DE-SC0014176 – Tunable Oxygen Reduction Electrocatalysis by Phenazine-Modified Carbons

Project Goals

This project aims to systematically investigate the fundamental interfacial chemistry that underlies the four-electron, four-proton oxygen reduction reaction (ORR) mediated by heteroatom-doped graphitic carbon electrodes. Heteroatom-doped (Fe, N, etc.) graphitic carbons have emerged as a rich class of materials that are promising ORR catalysts in low temperature fuel cells because of their earth-abundant elements, extremely low cost, environmental harmlessness, and high tolerance to impurities in the fuel stream. However, despite decades of research, systematic efforts to improve the activity, selectivity, and durability of these catalysts has been hampered both by a complex heterogeneous distribution of potential N- and Fe-dopant active sites and by the inability to tune the local electronic structure and environment of the active site with molecular precision. Understanding the fundamental chemistry that influences the turnover-limiting and selectivity determining steps for ORR and other multielectron/multiproton electrocatalytic transformations requires new and innovative methods to prepare heteroatom active sites with molecular precision on carbon surfaces.

We have developed a new class of catalysts, graphite-conjugated phenazines (GCPs), that incorporates molecularly well-defined, highly-tunable active sites into heterogeneous graphite surfaces by condensing *o*-phenylenediamines with *o*-quinone moieties that occur natively on graphitic carbon surfaces. This mild condensation proceeds with high fidelity to generate carbon surfaces modified with phenazine units, which are active ORR catalysts in alkaline electrolyte. This synthetic method enables systematic control over the electronic structure and local environment of the active site via synthetic modification of the diamine precursor. Using this platform, we aim to (1) enhance catalysis via functional group substitution of the phenazine active site, (2) enhance catalysis via metal ion coordination to phenazine active sites, (3) investigate homogeneous molecular models of surface phenazine active sites, (4) expand GCP chemistry to catalytic systems that undergo thermal catalysis rather than electrocatalysis and (5) probe fundamental aspects of electronic delocalization and active site-surface coupling and their influences on metal coordination environment, applied ligand field, catalytic performance as well as reactive intermediates.

Over the course of the project, we demonstrated that the electronic properties of the phenylene diamine precursor significantly affect the rate of ORR and developed methods for incorporating metal ions into the GCP via phenanthrolinediamine ligands. These developments allowed us to expand our efforts into areas of catalysis such as CO_2 reduction and hydrogen evolution in addition to ORR. Also, we have further developed our understanding of the electron transfer properties of these materials, demonstrating that GCP sites are hosts for inner-sphere electron transfer, directly analogous to sites on metallic surfaces. Additionally, we have demonstrated that graphitic carbons are active metal-free hydrogenation catalysts, and that incorporating solubilizing ligands onto carbon nanoparticles has a negligible impact on surface active sites. All of these results are key steps in taking GCP chemistry to thermal systems. We have also started to look at additional aspects of coordination chemistry at graphite-conjugated metal complexes such as variations in ligand donor/acceptor properties. We intend to observe variations in the thermodynamics and kinetics of such reactions and draw conclusions about the strength of any applicable ligand fields at conjugated metal centers for comparison to their molecular analogues. In parallel we also plan to investigate catalytic intermediates on graphite-conjugated catalysts to further enumerate the impact of strong electronic coupling on reactive catalytic sites. Overall, we plan to rationally design graphite-conjugated active sites, metal-containing and metal-free, for a range of catalytic applications, both thermal and electrochemical.

Project Accomplishments

We developed a general strategy for modification of carbon electrodes via site-selective condensation of *o*-phenylenediamine precursors to edge plane *o*-quinone moieties ubiquitous on graphitic carbons. The methodology described here is widely applicable for *o*-diamine-containing organic molecules, charged moieties, and coordination compounds. These graphite-conjugated catalysts (GCCs) can be prepared on virtually any graphitic carbon.

Both X-ray photoelectron spectroscopy (XPS) and N K-edge X-ray absorption near edge structure (XANES) validate the fidelity of the surface chemistry of GCCs. An excellent match is observed between the spectrum of GCCs and their molecular analogs, establishing the fidelity of this method of surface modification. Linear sweep voltammetry (LSV) of GCCs functionalized with substituted diamine precursors (GCC-phenazine) showed reduced overpotentials for ORR electrocatalysis relative to that of unmodified carbon surfaces. Electron-withdrawing substituents increased the potential of onset for ORR, as shown by the LSV, establishing molecular tunability. With these promising ORR catalytic results in hand, we extended our methodology to transition-metal-based surface electrocatalysts. Condensation of *fac*-Re(5,6-diamino-1,10-phenanthroline)$(CO)_3Cl$ to graphitic carbon generates graphite-conjugated rhenium (GCC-Re) catalysts that display catalytic CO_2 reduction currents greater than 50 mA/cm^2 (normalized to geometric surface area) with 96 ± 3% Faradaic efficiency for CO production.

We sought to expand from flat carbon surfaces to high-surface area colloidal carbon nanoparticle (NP) supports, allowing for increased loading while retaining access to the band states of carbon. We targeted surface carboxylic acids on graphitic NPs to generate colloids with amide-linked capping ligands of various lengths (C_3, C_8, and C_{18} linear chains) to study the impact of capping ligands on NP catalysts. The surface packing density remained constant at 0.9 ± 0.1 ligands nm^{-2} for all ligand lengths, sidestepping the ligand dynamic equilibrium that exists for metal NPs. The steric bulk of the ligand shell minimally affected the catalytic activity of the NPs, suggesting that there is no fundamental dichotomy between colloidal solution stability and robust catalytic activity.

While carbon is a promising transition-metal free heterogeneous catalyst in *non-electrochemical* systems, its activity under mild, synthetically applicable conditions has generally been limited to aerobic oxidation chemistry. We therefore investigated harnessing this oxidative reactivity to allow access to *reductive* chemistry. Upon treatment with hydrazine, we found that graphitic carbon was irreversibly modified with significant N-content in the formed material, and generates *diimide*, N_2H_2, which hydrogenates olefins to the corresponding alkanes. We demonstrated that surface modification of carbon is in fact critical for catalysis, with attenuation of the native aerobic oxidative reactivity of carbon enabling highly chemoselective alkene hydrogenation. This work showcases the ability of graphitic carbon and modified graphitic carbon to perform a plethora of useful synthetic reactions.

Leveraging the molecularly well-defined nature of GCCs, we pursued detailed microkinetic and theoretical investigations into our most ORR-active GCC. Experimentally, we observed two distinct current-potential (Tafel) regimes in ORR catalysis: low overpotentials exhibited a 60 mV/decade relationship consistent with a *reversible* one-electron transfer being rate-limiting, whereas higher reducing potentials showed a 120 mV/dec relationship indicative of rate-limiting *irreversible* single electron transfer. Furthermore, we observed a slightly depressed first-order O_2 partial pressure dependence and a minimal order dependence in proton.

In collaboration with the Van Voorhis group at MIT, we applied hybrid density functional theory (DFT) in order to better model ORR on GCCs. This revealed that O_2 binds to a semi-localized doublet state. At the lower overpotential, an initial reversible outer-sphere ET transiently forms superoxide prior to O_2 binding. However, this process occurs in a concerted fashion at higher potentials, consistent with our experimental data. In addition to this analysis, O_2 was modelled using simple descriptor analysis and placed on a volcano-like plot of -O and -OH binding strengths. As predicted by our mechanistic model, the GCC catalysts lie on the ‘associative’ leg, with similar activity to metallic silver. Therefore, this study demonstrates that in order to increase activity for molecularly designed N-doped carbons, a strategy is needed to break scaling relations e.g. a multi-site O_2 reduction manifold.

We have also discovered that the unique conjugated linkage formed between GCC sites and carbon electrodes leads to a distinct mechanism of ET. Electrochemical and spectroscopic studies led to three key observations, from which we constructed a mechanistic model.

Our first observation is that in the absence of bond cleavage or formation, redox features are not observed at GCC sites. Cyclic voltammograms (CVs) of $[Ru^{II}(dmbpy)_2(phen)]^{2+}$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine, phen = 1,10-phenanthroline) display a reversible Ru(III/II) wave when dissolved in solution or anchored to an electrode surface through an insulating aliphatic linkage. Remarkably, conjugating this Ru center to the graphite surface causes the redox waves to disappear. Similarly, CVs of phenazine in aprotic acetonitrile electrolyte show a reversible one-electron redox wave, but a phenazine unit conjugated to a carbon electrode shows no redox waves.

The inability to do outer-sphere ET to these GCC sites is consistent with electronic coupling of the molecular fragment with the electrode, which causes GCC sites to behave analogously to metallic electrodes. Upon application of potential to a metallic electrode, the ensuing interfacial field gradient raises the Fermi level of the solid *and* the energy levels of surface atoms in synchrony; the energy separation between the donor/acceptor states of the surface atoms and the Fermi level remain the same irrespective of the applied potential. Thus, on a GCC electrode, varying the applied potential does not change the *difference* in the potential between the electrode and the GCC site, precluding outer-sphere ET.

Our second observation is that GCC sites *do* undergo ET if the ET process is coupled to forming or breaking a bond with an ion in solution. Although CVs of GCC-phenazine do not display redox features in aprotic electrolyte, they display reversible redox waves when a proton source is present. Additionally, $[Rh^{III}Cp^*(phenda)Cl]^+$ (Cp* = pentamethylcyclopentadienyl), which loses a chloride upon reduction of the metal center, also gives rise to a redox feature associated with chloride when conjugated to graphite.

In both of these cases, ion transfer is driving ET. Though there is negligible potential drop between the electrode and the GCC site, there *is* a potential drop between the GCC and the solution. Therefore, applying potential alters the driving force for *ions* to transfer between the GCC site and the solution, provided that the surface site is able to bind the ion in question. This potential-dependent ion association and dissociation leads to compensatory electron flow from the external circuit, which we observe as a redox wave.

Our last observation was *in situ* XANES data that indicated the oxidation state of the Rh remains constant throughout the redox event for GCC-Rh. This observation has important implications on catalyst design; since the oxidation state of the GCC site can remain constant throughout an ET process, the valency and reduction potential of the molecular analogue do not directly dictate the rate and driving force for elementary and catalytic redox reactions at GCCs. Instead, redox chemistry at GCCs must be driven by the binding strength of substrates and intermediates with the surface sites.

In summary, the reactivity patterns of GCCs mimic those of metallic surface sites. At metal surface sites, ET proceeds exclusively via inner-sphere mechanisms in which electron flow is driven by ions or molecules crossing the double layer. As a result, ET is only observed when bonds are made or broken at metallic surface sites, and no ET occurs when no species can adsorb to the surface. Our data suggest that ET at graphite-conjugated molecules also proceeds exclusively via inner-sphere pathways, making GCCs mechanistically indistinguishable from authentic metallic surfaces.

Graphite Conjugated Prophyrins

We have expanded the scope of GCCs to a new ligand platform that can support earth-abundant yet labile first-row transition metals. To that end, we synthesized a diaminoporphyrin that readily condenses onto graphitic carbon surfaces. Porphyrins are an ideal platform as they strongly chelate metals in the central cavity resulting in remarkable stability of the resulting complex. Furthermore, metalloporphyrins demonstrate an enormous breadth of reactivity in both synthetic and biological systems where they are known catalysts for CO_2 reduction, O_2 reduction, oxidative C-H activation and nitrene transfer, among many other reactions. As a result, the development of this GCC-porphyrin platform opens up a vast space for electrochemical and thermal catalytic studies as well as enabling numerous spectroscopic studies that previously remained elusive.

Before examining the emergent reactivity of the conjugated porphyrins, we sought to understand how conjugation impacts the catalytic behavior relative to similar porphyrins that were heterogenized with linkages that do not confer strong electronic coupling. Heterogenized porphyrins have been used for electrocatalytic purposes for over sixty years and display a remarkable diversity in reactivity depending on the surface ligation methodology. While this variation in activity has been observed for numerous metalloporphyrins, the origin remains largely unknown. We hypothesized that the electronic interaction of the porphyrin with the surface may be a contributing factor to the observed variation in reactivity. In order to test this hypothesis, we ligated cobalt tetraphenylporphyrin (CoTPP) to glassy carbon surfaces following two methods that provide strong and weak electronic coupling. The strongly-coupled system consists of the conjugated porphyrin, GCC-CoTPP, whereas the weakly-coupled system consists of CoTPP ligated via an amide linkage to the surface, called Amide-CoTPP. Both systems were rigorously characterized by spectroscopic and electrochemical techniques.

We evaluated the oxygen reduction activity of the two systems as probe for the impact of electronic coupling on defining catalytic activity. Both systems display activity for oxygen reduction in aqueous acidic media, however, the strongly coupled GCC-CoTPP shows an earlier onset potential by 60 mV as compared to the weakly-coupled Amide-CoTPP. Both systems reach similar peak current densities, suggesting similar product fractionation. Indeed, quantification of the peroxide byproduct reveals that the two catalysts show nearly identical selectivity for the four-electron reduction to water. In order to determine the relative rates of the oxygen reduction reaction on a per-site basis, we quantified the surface coverage of cobalt for each catalyst and determined the turnover frequencies for each catalyst. In the activation-controlled region, we found that GCC-CoTPP displays an order of magnitude rate enhancement relative to the weakly coupled Amide-CoTPP. This result reveals that the electronic coupling engendered by the linkage chemistry directly impacts the catalytic rate and should be considered when designing new methods for the heterogenization of molecular catalysts.

Molecular Control of PCET

Our continued interest in investigating the fundamentals of inner-sphere chemistry at GCC sites motivated our pursuit for understanding how the installation of other PCET-active groups onto the GCC scaffold would influence the resulting electrochemistry. We surmised that the potential of the redox wave would scale with the pK_a of the PCET-active group and the redox potential of the electron donor/acceptor. In general, the redox potential of a PCET process (E_{PCET}) can be described as the sum of the proton transfer [2.3RT/F x $pK_a(BH^+)$ – 2.3RT/F x pH] and electron transfer (E_{ET}) steps using a thermochemical cycle (equation 1).

$$E_{\text{PCET}} = \frac{2.3RT}{F} pK_a(BH^+) - \frac{2.3RT}{F} pH + E_{\text{ET}} \qquad \textbf{(1)}$$

To study the influence of other PCET active groups, we prepared a variety of graphite-conjugated phenazine complexes with substitution on the backbone of the diamine precursors.

Installation of phenolic-functional groups (GCC-phen-*m*/*o*-OH) resulted in the formation of a new surface confined redox wave near -0.2 V vs NHE in addition to the standard phenazine PCET process near -0.8 V vs NHE. Unlike the molecular analogue of the phenolic GCC, the redox process for GCC-phen-*m*-OH displays reversible waves for both phenazine and phenol-based PCET. Preparation of the ethoxy analogue, GCC-phen-*m*-OEt, only gives rise to one redox process at -0.8 V vs NHE which we attribute to PCET at the phenazine linkage. Collectively, these results confirm our hypothesis that installation of other PCET active groups will result in the appearance of additional surface-confined PCET waves.

To our surprise, the appearance of new PCET waves is not limited to molecules that are well-known to be PCET active. The installation of aryl-carboxy and aniline GCCs also results in new and unique surface confined waves that all exhibit a pH dependence that confirms $1H^+/1e^-$ redox processes. Interestingly, a linear correlation exists between the position of the redox process (E_{PCET}) and pK_a of the molecular analogue. The slope of this correlation, 59 mV/pKa, is identical to the 2.3RT/F constant in equation 1. As such, these results suggest that variations in the pK_a of the GCC does not influence the redox potential of the GCC (E_{ET}).

To understand the origins of these correlations, we developed a model of PCET at GCC electrode surface sites. The metallic carbon electrode consists of filled states (gray) and unfilled states (light blue), and the transition between the two corresponds to the Fermi level of the electrode. The Fermi level, denoted E_F, is the electrochemical potential of the electrons in the electrode. This value has contributions from the chemical potential of electrons in the solid (approximated by the work function of the solid) and the electrostatic potential drop between the electrode and solution. Raising E_F by charging the carbon electrode increases the magnitude of the electrostatic potential drop across the double layer but leaves the chemical potential of the electrons in the solid largely unchanged. The high degree of electronic coupling between the conjugated site and the electrode ensures that changes in E_F lead to similar changes in the electrostatic potential of the conjugated surface functional groups. The rough spatial extent of the electrical double layer (EDL) is demarcated with a dotted vertical line, and the dotted blue line represents the electrostatic potential drop across the double layer. This electrostatic potential drop is the difference between E_F and the potential of zero free charge (PZFC) of the electrode (E_{PZFC}). The overall PCET process can therefore be thought of as a surface protonation/deprotonation event driven by the electric field ($E_F - E_{\text{PZFC}}$). Changes in the electrode modulate the field strength and the position of the wave reflects how more acidic functional groups require a larger field strength to become protonated.

The lack of change of (E_{ET}) between different GCCs suggests that the electron transfer component of equation 1 is unaffected by local changes in phenazine substitution. Specifically, we propose that electron transfer occurs to the graphitic solid, which should be unaffected by pH or the functional groups on the surface. Indeed, these results confirm that the potential for PCET at graphite conjugated sites can be approximated by the redox potential of the graphitic material (E_{PZFC}) and the pK_a of the molecular analogue by using equation 2.

$$E_{\text{PCET}} = \frac{2.3RT}{F} pK_a(molecular - analogue) - \frac{2.3RT}{F} pH + E_{\text{PZFC}} \qquad \textbf{(2)}$$

The overall PCET process can be visualized within a partial square scheme, which partitions the overall free energy for PCET (diagonal, black) as contributions from the proton transfer (horizontal, red) and electron transfer (vertical, blue) thermochemistry. A remarkable feature of interfacial PCET square schemes is that the ET and PT driving force can be independently tuned via the identity of the metallic solid and the identity of the protic functional group, respectively. This independence is distinct from square schemes for PCET on small molecules, where the proximity between the proton and electron donor/acceptor states renders independent tuning to be difficult if not impossible. These insights provide an important design criterion for tuning the thermochemistry of PCET at interfaces. For example, our model suggests that the rational tuning of the thermochemistry of important PCET intermediates in electrocatalysis can be envisaged through changing the work function of the material (E_{PZFC}) or via changes in the surface acidity.

Training and professional development fostered by the project

This project has provided a rich graduate and postdoctoral training platform. Our work on the catalytic chemistry of carbon surfaces has already comprised a significant fraction of the thesis of two 2 former graduate students (Megan Jackson and Sterling Chu) and is a significant component of the ongoing thesis work of 5 additional graduate students (Corey Kaminsky, Seokjoon Oh, Travis Marshall-Roth, Jeff Rosenberg, Noah Lewis). The project also comprises a majority of the research work of four postdoctoral fellows (Tomohiro Fukushima (former), Alexander Murray (former), Micheal Pegis (former), and Patrick Smith (former)).

Dissemination of the research results

The work has been disseminated to the community through 6 primary research publications:

Fukushima, T; Drisdell, W.; Yano, J.; **Surendranath, Y.** *J. Am. Chem. Soc.* **2015**, *137,* 10926–10929.
"Graphite-Conjugated Pyrazines as Molecularly Tunable Heterogeneous Electrocatalysts."

The work has also been highlighted by the *Journal of the American Chemical Society*'s "JACS Spotlight" and the MIT News through a press release.

Oh, S.; Gallagher, J. R.; Miller, J. T.; **Surendranath, Y.** *J. Am. Chem. Soc.* **2016**, *138*, 1820–1823.
"Graphite-Conjugated Rhenium Catalysts for Carbon Dioxide Reduction."

The work has been highlighted by DOE BES Catalysis Science BRN.

Chu, S. B.; Fukushima, T.; **Surendranath, Y.** *Chem. Mater.* **2017**, *29*, 495–498.
"Minor Impact of Ligand Shell Steric Profile on Colloidal Nanocarbon Catalysis"

Murray, A. T.; **Surendranath, Y.** *ACS Catal.* **2017**, *7*, 3307–3312.
"Reversing the Native Aerobic Oxidation Reactivity of Graphitic Carbon: Heterogeneous Metal-Free Alkene Hydrogenation"

Ricke, N.; Murray, A. T.; Shepherd, J.; Welborn, M.; Fukushima, T.; Van Voorhis, T.; **Surendranath, Y.** *ACS Catal.* **2017**, *7*, 7680–7687.
"Molecular-Level Insights into Oxygen Reduction Catalysis by Graphite-Conjugated Active Sites"

Jackson, M. N.; Oh, S.; Kaminsky, C. J.; Chu, S. B.; Zhang, G.; Miller, J. T.; **Surendranath Y.** *J. Am. Chem. Soc.* **2018**, *140*, 1004–1010.
"Strong Electronic Coupling of Molecular Sites to Graphitic Electrodes via Pyrazine Conjugation"

The work has also been highlighted by the *C&E News, DOE BES, and* featured in the DOE BES Catalysis Science BRN.

Kaminsky, C. J.; Wright, J.; **Surendranath, Y.** *ACS Catal.* **2019**, *9*, 3667–3671.
"Graphite-Conjugation Enhances Porphyrin Electrocatalysis"

The work has also been provided as a highlight to DOE BES program managers.

Jackson, M. N.; Pegis, M. L.; **Surendranath, Y.** *ACS Cent. Sci.* **2019**, 5, 831-841.
"Graphite-Conjugated Acids Reveal a Molecular Framework for Proton-Coupled Electron Transfer at Electrode Surfaces"

The work has also been highlighted by the *MIT NEWS, and ACS Central Science.*

Jackson, M. N.; Kaminsky, C.; Oh, S.; Melville, J. F.; **Surendranath, Y.** *J. Am. Chem. Soc.* **2019**, *141*, 14160–14167.
"Graphite Conjugation Eliminates Redox Intermediates in Molecular Electrocatalysis"

The work has also been highlighted by the *C&E News, and Science.*

Jackson, M. N.; **Surendranath, Y.** *Acc. Chem. Res.* **2019**, *52*, 3432–3441.
"Molecular Control of Heterogeneous Electrocatalysis through Graphite Conjugation"

The work has also been the subject of provisional patent application:

Surendranath, Y.; Fukushima, T; O'Reilly, M., E.; Oh, S.; Murray, A. T.; Kaminsky, C. J.; Chu, S. B.; Jackson, M. N. Molecularly Tunable Heterogeneous Catalysts by Edge Functionalization of Graphitic Carbons. U.S. Provisional Patent Application No: 62/205,357.

The PI has also disseminated the work through many invited talks:

Symposium on Applied Chemistry, Max Planck Institute for Chemical Energy Conversion – Berlin, Germany, April 2019.

University of Chicago, Department of Chemistry – Chicago, IL, April 2019.

Keynote Lecture, 24th Special Topical Meeting of the International Society of Electrochemistry – Merida, Mexico, April 2019.

American Chemical Society National Meeting, Symposium on Chemistry at the Interface of Solution-processed Inorganic Materials – Orlando, FL, April 2019.

American Chemical Society National Meeting, Harry Gray Award for Creative Work in Inorganic Chemistry by a Young Investigator: Symposium in honor of Jillian Dempsey – Orlando, FL, March 2019.

Bio-Inspired Solar Energy Program, Canadian Institute for Advanced Research – Princeton, New Jersey, March 2019.

Mohammed VI Polytechnic University – Ben Guerir, Morocco, March 2019.

California Institute of Technology, Department of Chemistry – Pasadena, CA, March 2019.

University of California, San Diego, Department of Chemistry – La Jolla, CA, March 2019.

Columbia University, Department of Chemistry – New York City, NY, February 2019.

Texas A&M University, Department of Chemistry – College Station, TX, February 2019.

University of Texas at Austin, Department of Chemistry – Austin, TX, February 2019.

E. B. Wilson Prize Lecture, Harvard University, Department of Chemistry – Cambridge, MA, January 2019.

University of Pittsburgh, Department of Chemistry – Pittsburgh, PA, January 2019.

NanoGe Conference on New Advances in Materials Research for Solar Fuels Production – Terramolinos, Spain, October 2018.

Instituto Catalonia in Quimica (ICIQ) – Terragona, Spain, October 2018.

Ecole Polytechnique Federale de Lausanne (EPFL), Department of Chemistry and Chemical Engineering – Lausanne, Switzerland, October 2018.

University of Illinois Urbana-Champaign, Department of Chemistry – Urbana, IL, October 2018.

Frontiers of Molecular Engineering, Institute for Molecular Engineering, University of Chicago – Chicago, IL, September 2018.

Third International Seminar in Electro Chemistry – Curitiba, Brazil, August 2018.
LightCHeC Summer School – Les Diablerets, Switzerland, August 2018.
Gerischer Electrochemistry Today Conference – Boulder, CO, August 2018.
Telluride Workshop: Molecular Chemistry in Electrochemical Energy Storage – Telluride, CO, July 2018.
University of Cambridge, Department of Chemistry – Cambridge, United Kingdom, June 2018.
Paris Diderot University, Department of Chemistry – Paris, France, June 2018.
PCET2018, 3rd International Conference on Proton Coupled Electron Transfer – Blowing Rock, NC, June 2018.
Uppsala University, Department of Chemistry – Uppsala, Sweden, May 2018.
Stanford University, Department of Chemistry – Stanford, CA, April 2018.
University of Wisconsin, Madison, Department of Chemistry – Madison, WI, April 2018.
Cornell University, Department of Chemistry – Ithaca, NY, March 2018.
University of North Carolina, Chapel Hill, Department of Chemistry – Chapel Hill, NC, March 2018.
29th Kavli Frontiers of Science Symposium – Irvine, CA, February 2018.
University of California, Irvine, Department of Chemistry – Irvine, CA, February 2018.
University of California, Santa Barbara, Department of Chemistry – Santa Barbara, CA, February 2018.
University of Southern California, Department of Chemistry – Los Angeles, CA, January 2018.
University of California, Los Angeles, Department of Chemistry – Los Angeles, CA, January 2018.
Purdue University, Department of Chemistry – West Lafayette, IN, January 2018.
Gordon Research Conference on Electrochemistry – Ventura, CA, January 2018.
Global Research Center for Environment and Energy Based on Nanomaterials Science (GREEN), National Institute for Materials Science – Tsukuba, Japan, October 2017.
Yale University, Department of Chemistry – New Haven, CT, October 2017.
University of California, Berkeley, Department of Chemistry – Berkeley, CA, September 2017.
American Chemical Society National Meeting, Symposium on Personal and Global Energy Conversion in Chemistry and Biology – Washington, DC, August 2017.
Penn Conference on Theoretical Chemistry, University of Pennsylvania – Philadelphia, PA, August 2017.
Telluride Solar Solutions Workshop – Telluride, CO, June 2017.
Boston College, Department of Chemistry – Chestnut Hill, MA, September 2016.
Michigan State University, Department of Chemistry – East Lansing, MI, September 2016.
Inorganic Chemistry Conference Erlangen, Friedrich-Alexander University – Erlangen, Germany, September 2016.
American Chemical Society National Meeting – Philadelphia, PA, August 2016.
Toyota Research Institute of North America – Ann Arbor, MI, August 2016.
New England Catalysis Society, Spring Meeting – Providence, RI, May 2016.
ExxonMobil Chemical Company – Baytown, TX, April 2016.
University of Oregon, Department of Chemistry and Biochemistry – Eugene, OR, April 2016.
American Chemical Society National Meeting – San Diego, CA, March 2016.
Gordon Research Conference on Renewable Energy: Solar Fuels – Tuscany, Italy, March 2016.
Gordon Research Conference on Electrochemistry – Ventura, CA, January 2016.
Gordon Research Conference on Renewable Energy: Solar Fuels – Tuscany, Italy, March 2016.
American Chemical Society National Meeting – San Diego, CA, March 2016.
University of Oregon, Department of Chemistry and Biochemistry – Eugene, OR, April 2016.
ExxonMobil Chemical Company – Baytown, TX, April 2016.

New England Catalysis Society, Spring Meeting – Providence, RI, May 2016.
Toyota Research Institute of North America – Ann Arbor, MI, August 2016.
American Chemical Society National Meeting – Philadelphia, PA, August 2016.
Inorganic Chemistry Conference Erlangen, Friedrich-Alexander University – Erlangen, Germany, September 2016.
Michigan State University, Department of Chemistry – East Lansing, MI, September 2016.
Boston College, Department of Chemistry – Chestnut Hill, MA, September 2016.
American Chemical Society National Meeting – San Francisco, CA, April 2017.

Students in the group have also disseminated the work at the following conferences:

Gordon Research Conference on Electrochemistry – Ventura, CA, January 2016.
Gordon Research Conference on Physical Organic Chemistry – Holderness, NH, June 2015.
Gordon Research Conference on Electron Donor Acceptor Interactions – Newport, RI, August 2016.
Gordon Research Conference on Inorganic Reaction Mechanisms – Galveston, TX, March 2017.
Gordon Research Conference on Inorganic Chemistry – Biddeford, ME, June 2018
3rd International Conference on Proton-Coupled Electron Transfer – Blowing Rock, NC, June 2018.
Gordon Research Seminar on Catalysis – New London, NH, June 2018
New England Catalysis Society, Fall Meeting – Cambridge, MA, December 2018
Gordon Research Conference on Chemical Reactions at Surfaces – Ventura, CA, February 2019.
Gordon Research Conference on Inorganic Reaction Mechanisms – Galveston, TX, March 2019.

Impact:

Impact on the development of the principal discipline of the project.

GCCs are a new class of surface catalyst, in that the catalytic site is strongly coupled to the band states of the bulk electrode. This is in contrast with existing methods for immobilizing molecular catalysts onto electrode surfaces. Numerous methods for appending molecular catalysts to electrode surfaces have been developed, ranging from those that utilize weak physisorption/electrostatic interactions to those that form strong covalent linkages. However, with rare exceptions, these methods connect the catalytic unit to the electrode surface through inert tethers that engender weak electronic coupling between the molecular active site and the delocalized states of the metallic electrode. As a result, catalysis is pinned to the reduction potential of the appended molecular catalyst, thus the driving force for the reaction is set by the selected molecular catalyst, not the applied electrode potential. However, GCCs exhibit strong electronic coupling to the band structure of the electrode and thus catalysis is no longer pinned to the reduction potential of the appended catalyst. As a result, the driving force for the reaction is set directly by the potential of the electrode. Thus, GCCs are unique in truly bridging molecular and heterogeneous catalysis by allowing for strong electronic coupling to band states of the solid to decouple reactivity from the reduction potential of the affixed catalyst while permitting virtually unlimited control over the local structure of the surface active site. To our knowledge, this is the first well-defined surface modified platform that provides for both of these attractive properties. This molecular-level control enables the rational parsing of surface effects on elementary chemical reactions – our work has elucidated the thermochemistry controlling proton-coupled electron transfer reactions on surface site – and on catalytic conversions, where we have unraveled the impact of electronic coupling on the rate and mechanism of catalytic reactions.

Impact on other disciplines

Our phenazine-modification strategy provides the rare opportunity to connect the traditionally disparate disciplines of molecular and heterogeneous catalysis since our method allows for molecular active sites to be synthetically tuned and incorporated into robust heterogeneous catalysts. Through kinetic studies comparing GCCs with molecular analogs, we have already been able to discern changes in catalyst mechanism, activity, and selectivity between the catalytic platforms, and we are continuing to investigate molecular analogues to gain insight into the origin of ORR activity in N-doped carbons. These studies, paired with DFT calculations in collaboration with Prof. Van Voorhis, will target the role of the band structure of carbon in modulating catalysis at surface-bound phenazines relative to discrete molecular analogs. These insights will be of great practical value to chemists, materials scientists, and engineers seeking to design more efficient catalysts. These studies also provide insight into fundamental questions relating to electronic structure and charge transfer properties at modified carbon surfaces that will be of great interest to chemists, physicists, and theorists.

Similarly, the synthetic modeling work on iron- and nitrogen-doped carbons as well as the GCC strategy more broadly provides another opportunity for cross over between the fields of molecular, heterogeneous catalysis and material science. The rising subfields of “single-atom” and “single-site” catalysis have been dominated by the material science community with limited input from the homogeneous catalysis community. Our various systems, either as models or as conjugated, well-defined surface sites will help bolster an understanding of the various structure-activity correlations that the material science community has been developing for catalyzing reactions such as ORR.

In addition, the robustness and fidelity of the surface chemistry uncovered as part of this work provides numerous opportunities for surface modification in diverse fields such as enzyme immobilization, environmental sensing, and graphene-based electronics.

Impact on technology transfer

The work has also been the subject of two provisional patent applications which will enable future development and scale-up of the technologies:

Surendranath, Y.; Fukushima, T; O’Reilly, M., E.; Oh, S.; Murray, A. T.;Kaminsky, C. J.; Chu, S. B.; Jackson, M. N. Molecularly Tunable Heterogeneous Catalysts by Edge Functionalization of Graphitic Carbons. U.S. Provisional Patent Application No: 62/205,357.