

*Catalysis and Chemical Transformations Program*

*Final Report*

**March 1, 2015**

**Project Title:** Biomimetic Catalysts Responsive to Specific Chemical Signals

**DOE grant number:** DE-SC0002142

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**Co-Principal Investigator:** L. Keith Woo, Andrew C. Hillier, Robert J. Angelici

**Total Budget:** \$1,116,000

**Period of Execution:** September 15, 2009 to September 14, 2014

**Year the Project Started:** 2009

## Abstract

### Part 1. Design of Biomimetic Catalysts Based on Amphiphilic Systems

The overall objective of our research is to create biomimetic catalysts from amphiphilic molecules. More specifically, we aim to create supramolecular systems that can be used to control the microenvironment around a catalytic center in a biomimetic fashion and apply the learning to construct supramolecular catalysts with novel functions found in enzymatic catalysts.

We have prepared synthetic molecules (i.e., foldamers) that could fold into helical structures with nanometer-sized internal hydrophilic cavities. Cavities of this size are typically observed only in the tertiary and quaternary structures of proteins but were formed in our foldamer prepared in just a few steps from the monomer. Similar to many proteins, our foldamers displayed cooperativity in the folding/unfolding equilibrium and followed a two-state conformational transition. In addition, their conformational change could be triggered by solvent polarity, pH, or presence of metal ions and certain organic molecules. We studied their environmentally dependent conformational changes in solutions, surfactant micelles, and lipid bilayer membranes.

Unlike conventional rigid supramolecular host, a foldamer undergoes conformational change during guest binding. Our study in the molecular recognition of an oligocholate host yielded some extremely exciting results. Cooperativity between host conformation and host–guest interactions was found to “magnify” weak binding interactions. In other words, since binding affinity is determined by the overall change of free energy during the binding, guest-induced conformational change of the host, whether near or far from the binding site, affects the binding. This study has strong implications in catalysis because enzymes have been hypothesized to harvest similar intramolecular forces to strengthen their binding with the transition state of an enzyme-catalyzed reaction.

The supramolecular and amphiphilic principles used in the foldamer catalysts were extended to a few other systems, particularly to interfacially cross-linked reverse micelles and micelles. These features enabled unusual catalytic features such as basic/nucleophilic catalysis under acidic conditions. We were able to create highly active metal nanoclusters catalysts whose local environment could be tuned by the organic framework. We were even able to create a “catalytic nanomachine” that grabs the substrate to the encapsulated Au clusters, which efficiently convert the substrate to the product that is rapidly ejected due to its different binding properties. Our research has important impacts on fundamental and applied energy-related sciences. On the fundamental level, it tests important biocatalytic principles on relatively simple synthetic systems and is expected to afford deeper understanding of biological catalysis. On the practical level, the research is anticipated to lead to “smart” catalysts and open up exiting applications in chemical analysis, reaction control, and materials synthesis.

## **Part 2. Electrochemical Reduction of CO<sub>2</sub>**

The primary objective of our research involving the electrochemical reduction of carbon dioxide is to apply a multidisciplinary approach toward developing a greater understanding of the problem of efficiently converting CO<sub>2</sub> to hydrocarbons through electrochemical routes. Our goal is to provide a better understanding of the principles that underlie the electrocatalytic reduction of CO<sub>2</sub> at electrode surfaces and the molecular pathways that lead to desired compounds. This understanding is essential for the design and development of new catalytic materials for the selective production of renewable feedstocks.

The electrochemical reduction of CO<sub>2</sub> involves the formation of various reaction products and adsorbed intermediates whose distribution depends upon the nature of the electrode material and the electrochemical conditions, including applied potential, solvent, and electrolyte, used during reduction. Our efforts are focused on developing a detailed picture of how these various parameters impact the reaction pathway for CO<sub>2</sub> reduction and to tune this reaction to favor the formation of specific products by careful selection of electrode materials and reaction conditions. Our experimental plan includes a detailed examination of the electrode material as well as a quantitative evaluation of the reaction conditions using several in-situ analysis tools that give a direct measure of adsorbed and solution species that appear during CO<sub>2</sub> reduction.

During the first year of funding for this aspect of the project, we have developed an on-line electrochemical measurement tool utilizing membrane-introduction mass spectrometry to detect reactions products directly during the electrochemical reduction of CO<sub>2</sub> on various sputtered electrode materials. In addition, we have examined the role of a selection of different electrode compositions (including single component and binary electrodes) on product distributions.

## Description of Results

### (a) Research Accomplishments

#### Part 1. Design of Biomimetic Catalysts Based on Amphiphilic Systems

**1.1.** Oligocholate foldamers with different numbers and locations of guanidinium–carboxylate salt bridges were synthesized. The salt bridges were introduced by incorporating arginine and glutamic acid residues into the foldamer sequence. The conformations of these foldamers were studied by fluorescence spectroscopy in homogeneous solution, anionic and nonionic micelles, and lipid bilayers. Environmental effects instead of inherent foldability were found to dominate the folding. As different noncovalent forces become involved in the conformations of the molecules, the best folder in one environment could turn into the worst in another. Preferential solvation was the main driving force for the folding of oligocholates in solution. The molecules behaved very differently in micelles and lipid bilayers, with the most critical factors controlling the folding–unfolding equilibrium being the solvation of ionic groups and the abilities of the surfactants/lipids to compete for the salt bridge. These results were published as a *J. Am. Chem. Soc.* full paper in 2010. Different micelles were also found to strongly affect the conformations of the foldamers, as shown in a *J. Org. Chem.* full paper in 2012 and an invited review published on *Acc. Chem. Res.* in 2013.

Rigid supramolecular hosts have been favored traditionally by chemists because of their perceived benefits in binding affinity. The tradition traces back to Fischer’s lock–key theory and was reinforced by the principle of preorganization articulated by Cram. The idea of preorganization brought great advancement in supramolecular chemistry over the last several decades and is continued to be used to guide the design of biomimetic catalysts with molecular-recognition motifs. More recently there is increasing appreciation that most biomolecular hosts (e.g., proteins) are folded linear molecules and not as nearly as rigid as preorganized macrocyclic compounds commonly employed by supramolecular chemists. It is perplexing that, if conformational mobility really represents a disadvantage to high-affinity binding, decades of efforts by chemists yielded mostly (rigid) synthetic supramolecular hosts no matching for their (less rigid) biological counterparts. Is it possible that chemists, in our efforts of rigidifying the synthetic hosts, have wandered away from certain critical elements for success? In a communication published on *J. Am. Chem. Soc.* in 2011, we reported several glutamate-functionalized oligocholate foldamers that bound  $\text{Zn}(\text{OAc})_2$ , guanidine, and even amine compounds with surprisingly high affinities. The conformational change of the hosts during binding was crucial to the enhanced binding affinity. The strongest cooperativity/synergism between the conformation and guest-binding occurred when the hosts were unfolded but near the folding–unfolding transition. These results suggest that high binding affinity in molecular recognition may be more easily obtained from large hosts capable of strong cooperative conformational changes instead of those with rigid, preorganized structures.

The performance of a catalyst is determined by both the active site and its environment. The principle is most beautifully demonstrated by enzymes that use the protein framework to control the polarity, acidity/basicity, size, shape, chirality of the active site, and, ultimately, the activity/selectivity of the catalyst. Following our recent success to prepare interfacially cross-linked reverse micelles (ICRMs) and surface-cross-linked micelles (SCMs), we turned these oil-

and water-soluble organic nanoparticles into powerful platforms to investigate environmentally controlled catalysis.

The ICRMs of a triallylammonium surfactant afforded organic nanoparticles with introverted cationic groups. The cross-linked reverse micelles catalyzed size-selective biphasic reaction between sodium azide and alkyl bromides. Size selectivity of up to 9:1 was obtained for alkyl bromides with similar structures. The selectivity was influenced strongly by the size of the water pool and proposed to happen as a result of the “sieving” effect of the alkyl corona. The results were published on *Org. Lett.* in 2012. Later on, the same ICRMs were found to encapsulate palladium nanoparticles within their hydrophilic cores and protect them in catalytic reactions. Good to excellent yields were obtained in the Heck coupling of a range of alkyl acrylates and iodobenzenes. The catalytic activity of the palladium nanoparticles was maintained in several repeated runs. These results were published as a full paper on *Helvetica Chimica Acta* in 2012.

Additionally, the ICRMs turned out as unusual templates for nanomaterials synthesis by extracting anionic metal salts such as tetrachloroaurate into the hydrophilic interior. The bromide counterions were established as the reducing agent in the template synthesis. The reduction of tetrachloroaurate was proposed to happen through ligand exchange on the aurate by the bromide ions, reductive elimination of halogen, and disproportionation of the Au(I) intermediate. The size of the gold clusters could be tuned rationally by the water-to-surfactant ratio ( $W_0$ ) and the reducing agent. Monodisperse Au<sub>4</sub> and Au<sub>9–10</sub> clusters as well as larger Au<sub>18</sub> and Au<sub>23</sub> clusters were obtained from the ICRM templates. These results were published as a full paper on *Langmuir* in 2012. In a communication on *ACS Catal.* in 2014, we reported that gold clusters encapsulated within the ICRMs catalyzed hydroamination of alkynes at room temperature instead of at 100 °C commonly required for gold nanoparticles. Different metal oxides introduced into the micelle core by sol–gel chemistry interacted with the gold clusters and modulated their catalysis, with silicon oxide being the most effective co-catalyst.

Creation of synthetic catalysts with enzyme-like behavior is challenging despite strong interest in such systems. In a communication published on *J. Am. Chem. Soc.* in 2014, we reported that extraction of tetrachloroaurate into the hydrophilic core of ICRM produced an artificial “metalloenzyme” with highly unusual catalytic properties. The ICRM pulled the substrate toward the catalytic metal, which converted it efficiently to the product that was rapidly ejected. These features enabled greatly reduced catalyst loading (30–100 times lower than typical levels used in literature examples), constant high reaction rate throughout the course of the reaction, lack of the hydrolyzed side product, and substrate selectivity unobserved in conventional gold catalysts.

ICRMs readily accommodated anionic gold and palladium metal salts in their ammonium-lined hydrophilic cores and allowed facile control of the metallic composition, as well as the metal oxides in the vicinity of the metals. In a full paper published on *New. J. Chem.* in 2015, we reported that deposition onto a solid support (P25 TiO<sub>2</sub>) followed by thermal treatment of Pd–Au-containing ICRMs yielded bimetallic nanoparticle heterogeneous catalysts through the controlled release of metals from the ICRMs. The catalysts allowed efficient oxidation of benzyl alcohol under relatively mild conditions with minimal amounts of oxidant (hydrogen peroxide) in water without any organic solvent.

Cross-linking of a tripropargylated ammonium surfactant by a diazide cross-linker in the presence of Cu(I) catalysts yielded surface-cross-linked micelles (SCMs) as water-soluble nanoparticles.

Cross-linking had a profound impact on the properties of the micelles. The binding of 1-anilinonaphthalene-8-sulfonic acid (ANS) indicated that the SCMs contained two types of binding sites, favoring the polar and nonpolar excited states of the probe, respectively. The SCMs also shielded the excited states of ANS from solvent exposure better than the micelles of cetyltrimethylammonium bromide (CTAB). The SCMs inhibited the excited state proton transfer (ESPT) of a polyanionic probe, pyranine, more strongly than CTAB micelles. The ESPT of a more hydrophobic probe, 2-naphthol, was found to be influenced by the stronger surface basicity of the SCMs, as well as their better shielding of the probe from the aqueous phase than the CTAB micelles. The stronger surface basicity of the SCMs also enabled them to catalyze the hydrolysis of an activated phosphate ester at neutral pH better than CTAB micelles. These results were published as a full paper on *J. Colloid Interface Sci.* in 2013. In a paper published on *Chem. Commun.* in 2012, we reported that the SCMs could be used to encapsulate and solubilize conventional hydrophobic organometallic catalysts. The resulting water-soluble, catalyst-containing nanoparticles resembled “artificial metalloenzymes” with unusual selectivity toward terminal olefins and unique chain-length preference in catalytic hydrogenation.

Cross-linking the micelles of 4-dodecyloxybenzyltripropargylammonium bromide by 1,4-diazidobutane-2,3-diol in the presence of azide-functionalized imidazole derivatives yielded surface-cross-linked micelles (SCMs) with imidazole groups on the surface. The resulting water-soluble nanoparticles were found, by fluorescence spectroscopy, to contain hydrophobic binding sites. The imidazole groups promoted the photo-deprotonation of 2-naphthol at pH 6 and catalyzed the hydrolysis of *p*-nitrophenylacetate (PNPA) in aqueous solution at pH  $\geq 4$ . Although the overall hydrolysis rate slowed down with decreasing solution pH, the catalytic effect of the imidazole became stronger because the reactions catalyzed by unfunctionalized SCMs slowed down much more. The unusual ability of the imidazole–SCMs to catalyze the hydrolysis of PNPA under acidic conditions was attributed to the local hydrophobicity and the positive nature of the SCMs. These results were published as a full paper on *Org. Biomol. Chem.* in 2013. In a paper published on *Chem. Commun.* in 2014, we reported that the nucleophilic catalysis by a pyridyl group in ester/phosphate ester hydrolysis was modulated by the microenvironmental hydrophobicity around the catalyst on the SCM platform. The catalytic efficiency was enhanced thousands or tens of thousands of times and the activity was maintained well below the  $pK_a$  of the pyridyl group. In a paper published on *Angew. Chem. Int. Ed.* in 2012, we also showed that the SCM was a versatile platform to construct light-harvesting systems. Two self-assembling strategies (micellization and electrostatic attraction) and covalent capture were employed to construct a robust, inexpensive, efficient artificial light-harvesting nanoparticle. The synthesis was achieved by a one-pot reaction. A high density of the antenna chromophores was achieved without self-quenching and excimer formation, thus affording extremely efficient energy transfer. These features potentially could be highly useful to construct novel photocatalytic systems mimicking the natural photosynthetic complex.

Transition metal-catalyzed reactions in water have attracted significant research attention in recent decades. In a full paper recently submitted to *New. J. Chem.*, we reported the synthesis of a cholate-functionalized phosphine ligand and its application in heterogeneous palladium-catalyzed Heck cross-coupling reactions. The facially amphiphilic cholate group was found to exert a strong influence on the activity and selectivity of the reactions, owing to its ability to create a hydrophobic microenvironment near the catalytic center. This feature resulted in a preference for hydrophobic substrates over less hydrophobic ones by the catalyst. In contrast, the enhanced selectivity and

reactivity was not observed in organic solvents or with a homogeneous control in which the catalyst was coordinated to water-soluble phosphines. Although our model procedure was demonstrated with the Heck reaction, the concept should be applicable to other systems. Our work demonstrated that creating local hydrophobic pockets near a catalytic center could be a powerful strategy to improve aqueous-based reactions, even for heterogeneous catalysts.

In a paper published on *RSC Adv.* in 2015, we reported that aqueous Sonogashira coupling between lipophilic terminal alkynes and aryl bromides or iodides gave moderate to high yields at 40 °C using readily available and inexpensive surfactants (2.0 w/v% in water) such as SDS and CTAB. The catalyst precursor was 2 mol% Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, and included a 5 mol% Cu(I) co-catalyst for aryl iodide substrates. Aryl-bromide reagents were found to be inhibited by iodide and Cu(I). Studies under Cu(I)-free conditions reveal two competing pathways. A deprotonation pathway gives rise to the traditional Sonogashira product, while a carbopalladation pathway produces enyne. The surfactant solution (SDS or CTAB) can be recycled up to three times for coupling between 1-octyne and 1-iodonaphthalene in the presence of CuI before the yields decrease.

## **Part 2. Electrochemical Reduction of CO<sub>2</sub>**

In a paper published on *Anal. Chem.* in 2013, we presented an experimental system that combines differential electrochemical mass spectrometry with hydrodynamic flow consisting of an impinging jet in a wall-tube configuration. This assembly allows simultaneous detection of electrochemical signals along with monitoring of dissolved gas species using differential electrochemical mass spectrometry under well-defined hydrodynamic conditions and over a wide range of mass transfer rates. The working electrode is deposited directly onto a thin, hydrophobic membrane, which also serves as the inlet to the mass spectrometer. This inlet provides extremely rapid mass detection as well as a high flux of products from the electrode surface into the mass spectrometer. The impinging jet is designed in a wall-tube configuration, in which the jet diameter is large compared to the electrode diameter, thus providing uniform and rapid mass transfer conditions over the entirety of the electrode surface. This combination of rapid detection and controllable flow conditions allows a wide range of hydrodynamic conditions to be accessed with simultaneous electrochemical and mass spectrometric detection of dissolved gas species, which is important in the analysis of a range of electrochemical reactions. The capabilities of this configuration are illustrated using a platinum-coated electrode and several electrochemical reactions, including ferrocyanide oxidation, proton reduction, and oxalic acid oxidation.

### **(b) Publication list in which DOE support is acknowledged**

1. Hongkwan Cho and Yan Zhao,\* "Environmental Effects Dominate the Folding of Oligocholates in Solution, Surfactant Micelles, and Lipid Membranes," *J. Am. Chem. Soc.* **2010**, *132*, 9890–9899. <http://dx.doi.org/10.1021/ja103694p>
2. Zhenqi Zhong, Xueshu Li, and Yan Zhao,\* "Enhancing Binding Affinity by the Cooperativity between Host Conformation and Host–Guest Interactions," *J. Am. Chem. Soc.* **2011**, *133*, 8862–8865. <http://dx.doi.org/10.1021/ja203117g>
3. Shiyong Zhang and Yan Zhao,\* "Effects of Micelle Properties on the Conformation of Oligocholates and Importance of Rigidity of Foldamers," *J. Org. Chem.* **2012**, *77*, 556–562. <http://dx.doi.org/10.1021/jo202156d>
4. Hui-Qing Peng, Yu-Zhe Chen, Yan Zhao, Qing-Zheng Yang,\* Li-Zhu Wu, Chen-Ho Tung, Li-Ping Zhang, Qing-Xiao Tong,\* "Artificial Light-Harvesting System Based on Multifunctional

- Surface Cross-Linked Micelles,” *Angew. Chem. Int. Ed.* **2012**, *51*, 2088–2092. <http://dx.doi.org/10.1002/anie.201107723>
5. Li-Chen Lee and Yan Zhao,\* “Size-Selective Phase-Transfer Catalysis with Interfacially Cross-Linked Reverse Micelles,” *Org. Lett.* **2012**, *14*, 784–787. <http://dx.doi.org/10.1021/ol203319w>
  6. Li-Chen Lee and Yan Zhao,\* “Interfacially Cross-Linked Reverse Micelles as Soluble Support for Palladium Nanoparticle Catalysts,” *Helvetica Chimica Acta* **2012**, *95*, 863–871. <http://dx.doi.org/10.1002/hlca.201100451>
  7. Shiyong Zhang and Yan Zhao,\* “Template Synthesis of Subnanometer Gold Clusters in Interfacially Cross-Linked Reverse Micelles Mediated by Confined Counterions,” *Langmuir* **2012**, *28*, 3606–3613. <http://dx.doi.org/10.1021/la204694c>
  8. Shiyong Zhang and Yan Zhao,\* “Artificial Metalloenzymes via Encapsulation of Hydrophobic Transition-Metal Catalysts in Surface Cross-Linked Micelles,” *Chem. Commun.* **2012**, *48*, 9998–10000. <http://dx.doi.org/10.1039/C2CC33012A>
  9. Geetika Chadha and Yan Zhao,\* “Properties of Surface-Crosslinked Micelles Probed by Fluorescence Spectroscopy and Their Catalysis of Phosphate Ester Hydrolysis,” *J. Colloid Interface Sci.* **2013**, *390*, 151–157. <http://dx.doi.org/10.1016/j.jcis.2012.09.042>
  10. Geetika Chadha and Yan Zhao,\* “Histidine-Functionalized Water-Soluble Nanoparticles for Biomimetic Nucleophilic/General-Base Catalysis under Acidic Conditions,” *Org. Biomol. Chem.* **2013**, *11*, 6849–6855. <http://dx.doi.org/10.1039/C3OB41485J>
  11. Yan Zhao,\* Hongkwan Cho, Lakmini Widanapathirana, and Shiyong Zhang, “Conformationally Controlled Oligocholate Membrane Transporters: Learning Through Water Play,” Invited article by *Acc. Chem. Res.*, **2013**, *46*, 2763–2772. <http://dx.doi.org/10.1021/ar300337f>
  12. Venkatachalam, S.; Angelici, R.; Woo, L. K.; Hillier, A. “High Rate Detection of Volatile Products Using Differential Electrochemical Mass Spectrometry: Combining an Electrode-Coated Membrane with Hydrodynamic Flow in a Wall-Tube Configuration.” *Anal. Chem.* **2013**, *85*, 6059–6065. <http://dx.doi.org/10.1021/ac400928p>
  13. Geetika Chadha and Yan Zhao,\* “Environmental Control of Nucleophilic Catalysis in Aqueous Solution,” *Chem. Commun.*, **2014**, *50*, 2718–2720. <http://dx.doi.org/10.1039/C3CC49593K>
  14. Li-Chen Lee and Yan Zhao,\* “Room-Temperature Hydroamination of Alkynes Catalyzed by Gold Clusters in Interfacially Cross-Linked Reverse Micelles,” *ACS Catal.*, **2014**, *4*, 688–691. <http://dx.doi.org/10.1021/cs401213c>
  15. Li-Chen Lee and Yan Zhao,\* “Metalloenzyme-Mimicking Supramolecular Catalyst for Highly Active and Selective Intramolecular Alkyne Carboxylation,” *J. Am. Chem. Soc.* **2014**, *136*, 5579–5582. <http://dx.doi.org/10.1021/ja501277j>
  16. Dairo, T. O.; Ellern, A.; Angelici, R. J.; Woo, L. K. “Addition of Amines to a Carbonyl Ligand: Syntheses, Characterization, and Reactivities of Iridium(III) Porphyrin Carbamoyl Complexes.” *Organometallics* **2014**, *33*, 2266–2276. <http://dx.doi.org/10.1021/om500189a>
  17. Roberts, G. M.; Lu, W.; Woo, L. K. “Aqueous Sonogashira Coupling of Aryl Halides with 1-Alkynes Under Mild Conditions: Use of Surfactants in Cross-Coupling Reactions.” *RSC Advances* **2015**, *5*, 18960–18971. <http://dx.doi.org/10.1039/c5ra00505a>
  18. Li-Chen Lee, Chaoxian Xiao, Wenyu Huang, and Yan Zhao,\* “Palladium–Gold Bimetallic Nanoparticle Catalysts by ‘Controlled Release’ from Metal-Loaded Interfacially Cross-Linked Reverse Micelles,” *New J. Chem.*, **2015**, *39*, in press. <http://dx.doi.org/10.1039/C4NJ01905A>
  19. Roberts, G. M.; Zhang, S.; Zhao, Y.; Woo, L. K. “Improving Reactivity and Selectivity of Aqueous-Based Heck Reactions by the Local Hydrophobicity of Phosphine Ligands.” *New Journal of Chemistry*, **2015**, submitted.



**(c) A total list of people who worked on the project**

**Graduate Student:**

Premkumar Rathinam Arivalagan (part time with additional support from Iowa State University teaching assistantship)

Geetika Chadha (part time with additional support from Iowa State University teaching assistantship)

Hongkwan Cho (part time with additional support from Iowa State University teaching assistantship)

Taiwo O. Dairo (part time with additional support from Iowa State University teaching assistantship)

Li-Chen Lee (part time with additional support from Iowa State University teaching assistantship),

Gina M. Roberts (part time with additional support from Iowa State University teaching assistantship)

Chia-Yu Shen (part time with additional support from Iowa State University teaching assistantship)

Subramanian Venkatachalam (part time with additional support from Iowa State University teaching assistantship)

**Postdoc:**

Xueshu Li (part time)

Zhefei Li (fully funded between 9/15/2010 and 3/09/2012)

Guozan Yuan (fully funded from 2010 to 2011)

Shiyong Zhang (part time),

**(d) An updated list of other support (current and pending)**

Yan Zhao

Current support (no overlap with the DOE project)

Cooperatively Folded Foldamer Hosts in Organic and Aqueous Solution, National Science Foundation, \$395,000, PI, from June 2013 to May 2016.

Pending support (None of these overlap with the DOE project)

Biomimetic Receptors for Small Hydrophobic Drugs, Carbohydrates, and Oligopeptides, NIH, PI, \$1.66 M, submitted in June 2014.

Synthetic Materials for Biofilm Inhibition, NSF, PI, \$688K, submitted in October 2014.

L. Keith Woo

Current support

None

Pending support (None of these overlap with the DOE project)

2015-17 NSF, “Catalyst Discovery and Development at the Chemistry-Biology Interface”: \$364,039 with L. Stanley (co-PI, Chem).

2015-19 DOE, “The Algal Crush Spread: Biofuels and Bioplastics”: \$10 M, co-PI with Eric Cochran (PI, CBE)

2015-18 DOE ARPA-E, “Efficient Electrochemical Heat Engines for Waste Energy Recovery”: \$2.25 M, co-PI with Wenzhen Li (PI, CBE)

Andrew C. Hillier

Current support (no overlap with DOE support)

Title: Highly Tunable Surface Plasmon Enhanced Optical Transmission Through Periodic Nanostructures, Sponsor: National Science Foundation, Dates of Contract Period: 9/01/12 - 8/31/15, Amount: \$449,000.

Pending support (no overlap with DOE support)

Title: Highly Tunable Plasmonic Enhancement of Surface Spectroscopies Using Diffractive Nanostructures, Sponsor: National Science Foundation, Dates of Contract Period: 9/01/15 - 8/31/18, Amount: \$474,698.

Robert J. Angelici

Current support

None

Pending support

None

## (e) Cost Status

<b>Account:</b> 4012001		<b>ICR Type:</b> MTDC		<b>Rev Code:</b> 04010 - FCG-DEPT OF ENERGY		
<b>Name:</b> DESC0002142-CBE-HILLIER		<b>ICR Rate:</b> 48.00%		<b>Sponsor Ref#:</b> DESC0002142		
<b>Acct Closed:</b> Y		<b>Acctnt:</b> 4 - NICHOLS TROY D		<b>Award Period:</b> Sep 15, 2010 - Sep 14, 2014		
<b>Structure:</b> Child		<b>PI:</b> HILLIER ANDREW C		<b>Pay Basis:</b> Cost reimbursement		
<b>Control Acct:</b> 4012104		<b>Fiscal Off:</b> MCKOWN KATHY		<b>Pay Method:</b> LOC DOE-Chicago		
<b>Org Unit:</b> 02 - COLLEGE OF ENGINEERING		<b>Proposal Nbr:</b>		<b>Cost Share:</b> 0.00		
<b>Org Dept:</b> 330 - CHEMICAL & BIOLOGICAL ENGR		<b>Award Nbr:</b> 004941-00002		<b>Award Type:</b> Grant		
<b>Award Status:</b> Closed		<b>Award Title:</b> BIOMIMETIC CATALYSTS RESP		<b>Sponsor:</b> DOE-US DEPARTMENT OF ENERGY		
<b>Mar Revenue:</b> \$0.00						
<b>Budget</b>		<b>Mar Expenses</b>	<b>Expenses Since Inception</b>	<b>Unspent Balance</b>	<b>Encumbrance</b>	<b>Balance</b>
<b>Object Rollup</b>						
SALARY/HOURLY ROLLUP		110,817.00	0.00	115,784.29	(4,967.29)	0.00 (4,967.29)
BENEFITS ROLLUP		21,005.00	0.00	15,469.41	5,535.59	0.00 5,535.59
DOMESTIC TRAVEL ROLLUP		3,000.00	0.00	3,186.26	(186.26)	0.00 (186.26)
STUDENT AID ROLLUP		9,203.00	0.00	23,745.00	(14,542.00)	0.00 (14,542.00)
SUPPLIES ROLLUP		20,653.00	0.00	10,812.13	9,840.87	0.00 9,840.87
HONORARIA/SERVICES ROLLUP		0.00	0.00	337.50	(337.50)	0.00 (337.50)
INDIRECT COST ROLLUP		74,628.00	0.00	69,883.00	4,745.00	0.00 4,745.00
<b>Account:</b> 4012114		<b>ICR Type:</b> MTDC		<b>Rev Code:</b> 04010 - FCG-DEPT OF ENERGY		
<b>Name:</b> DESC0002142-CHEM-WOO		<b>ICR Rate:</b> 48.00%		<b>Sponsor Ref#:</b> DESC0002142		
<b>Acct Closed:</b> Y		<b>Acctnt:</b> 4 - NICHOLS TROY D		<b>Award Period:</b> Sep 15, 2009 - Sep 14, 2014		
<b>Structure:</b> Child		<b>PI:</b> WOO LEE KEITH		<b>Pay Basis:</b> Cost reimbursement		
<b>Control Acct:</b> 4012104		<b>Fiscal Off:</b> OLSON NANCY M		<b>Pay Method:</b> LOC DOE-Chicago		
<b>Org Unit:</b> 04 - COLLEGE OF LIBERAL ARTS & SCIENCE		<b>Proposal Nbr:</b>		<b>Cost Share:</b> 0.00		
<b>Org Dept:</b> 183 - CHEMISTRY		<b>Award Nbr:</b> 004941-00003		<b>Award Type:</b> Grant		
<b>Award Status:</b> Closed		<b>Award Title:</b> BIOMIMETIC CATALYSTS RESPONSIV		<b>Sponsor:</b> DOE-US DEPARTMENT OF ENERGY		
<b>Mar Revenue:</b> \$0.00						
<b>Budget</b>		<b>Mar Expenses</b>	<b>Expenses Since Inception</b>	<b>Unspent Balance</b>	<b>Encumbrance</b>	<b>Balance</b>
<b>Object Rollup</b>						
SALARY/HOURLY ROLLUP		178,318.00	0.00	178,463.87	(145.87)	0.00 (145.87)
BENEFITS ROLLUP		29,469.00	0.00	25,351.62	4,117.38	0.00 4,117.38
DOMESTIC TRAVEL ROLLUP		4,500.00	0.00	200.00	4,300.00	0.00 4,300.00
FOREIGN TRAVEL ROLLUP		0.00	0.00	1,748.76	(1,748.76)	0.00 (1,748.76)
STUDENT AID ROLLUP		22,735.00	0.00	15,311.50	7,423.50	0.00 7,423.50
SUPPLIES ROLLUP		31,813.00	0.00	48,122.17	(16,309.17)	0.00 (16,309.17)
PRINTING/COPYING ROLLUP		0.00	0.00	201.90	(201.90)	0.00 (201.90)
HONORARIA/SERVICES ROLLUP		0.00	0.00	698.50	(698.50)	0.00 (698.50)
OTHER DIRECT EXP ROLLUP		5,671.00	0.00	0.00	5,671.00	0.00 5,671.00
INDIRECT COST ROLLUP		119,890.00	0.00	122,297.68	(2,407.68)	0.00 (2,407.68)
<b>Account:</b> 4012104		<b>ICR Type:</b> MTDC		<b>Rev Code:</b> 04010 - FCG-DEPT OF ENERGY		
<b>Name:</b> DESC0002142-CHEM-ZHAO		<b>ICR Rate:</b> 48.00%		<b>Sponsor Ref#:</b> DESC0002142		
<b>Acct Closed:</b> Y		<b>Acctnt:</b> 4 - NICHOLS TROY D		<b>Award Period:</b> Sep 15, 2009 - Sep 14, 2014		
<b>Structure:</b> Parent		<b>PI:</b> ZHAO YAN		<b>Pay Basis:</b> Cost reimbursement		
<b>Control Acct:</b> 4012104		<b>Fiscal Off:</b> OLSON NANCY M		<b>Pay Method:</b> LOC DOE-Chicago		
<b>Org Unit:</b> 04 - COLLEGE OF LIBERAL ARTS & SCIENCE		<b>Proposal Nbr:</b>		<b>Cost Share:</b> 0.00		
<b>Org Dept:</b> 183 - CHEMISTRY		<b>Award Nbr:</b> 004941-00001		<b>Award Type:</b> Grant		
<b>Award Status:</b> Closed		<b>Award Title:</b> BIOMIMETIC CATALYSTS RESPONSIVE TO SPECIFIC C		<b>Sponsor:</b> DOE-US DEPARTMENT OF ENERGY		
<b>Mar Revenue:</b> \$0.00						
<b>Budget</b>		<b>Mar Expenses</b>	<b>Expenses Since Inception</b>	<b>Unspent Balance</b>	<b>Encumbrance</b>	<b>Balance</b>
<b>Object Rollup</b>						
SALARY/HOURLY ROLLUP		211,387.00	0.00	199,137.41	12,249.59	0.00 12,249.59
BENEFITS ROLLUP		39,891.00	0.00	21,259.10	18,631.90	0.00 18,631.90
EQUIPMENT/COLLECTIONS ROLLUP		25,000.00	0.00	18,643.18	6,356.82	0.00 6,356.82
DOMESTIC TRAVEL ROLLUP		4,500.00	0.00	1,372.91	3,127.09	0.00 3,127.09
STUDENT AID ROLLUP		13,532.00	0.00	9,491.00	4,041.00	0.00 4,041.00
SUPPLIES ROLLUP		30,160.00	0.00	85,541.87	(55,381.87)	0.00 (55,381.87)
PRINTING/COPYING ROLLUP		0.00	0.00	57.04	(57.04)	0.00 (57.04)
HONORARIA/SERVICES ROLLUP		0.00	0.00	743.64	(743.64)	0.00 (743.64)
POSTAGE ROLLUP		0.00	0.00	6.82	(6.82)	0.00 (6.82)
OTHER DIRECT EXP ROLLUP		15,256.00	0.00	100.00	15,156.00	0.00 15,156.00
INDIRECT COST ROLLUP		144,572.00	0.00	147,944.99	(3,372.99)	0.00 (3,372.99)