Solvent Effects on Guest Orientation within a Self-Assembled Supramolecular Host and Exploration of chemistry on the Host Exterior Surface

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Use of supramolecular host-guest chemistry to mediate guest chemical reactivity is an exciting field of research, aiming to mimic and understand enzyme activity. The Raymond group has developed a series of self-assembling homochiral supramolecular M_4L_6 tetrahedron capable of acting as hosts for a variety of monocationic[1] and neutral[2] guest molecules (Figure 1), and as a molecular catalyst for a wide range of organic transformations.[3]

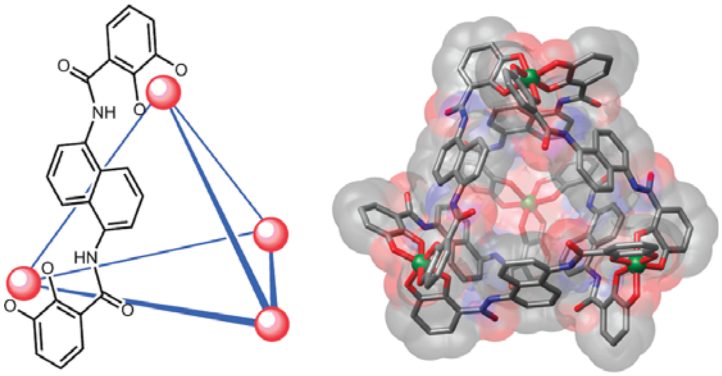

Figure 1. Left) Representation of a M_4L_6 assembly with only one ligand shown for clarity. (Right) A space-filling model of the assembly viewed toward a 3-fold axis.

However, the solvent dependent host-guest chemistry is much less addressed in literature. Our work showed that encapsulation of long chain ammonium proceeds with different orientations in different proportion of aqueous and organic solvents: organic solvent rich mixture favors encapsulation of positive-charged NMe_3^+ head and aqueous rich mixture favors encapsulation of hydrophobic alkyl tail. The experimental detail will be discussed.

Besides, we also demonstrate that the hydrophobic cavity of the self-assembled host is able to thermodynamically favor encapsulation of cationic guests that are stabilized by cation-π interaction with six naphthalene spacers.[4] This host also shows substrate size restriction, which only allows substrates below a certain size threshold to be encapsulated and undergo catalysis.[4]

To overcome this limitation, we are interested in expanding reactivity and catalysis to the exterior surface of the host molecule. Preliminary result shows that this idea is highly feasible. For example, we have shown that we can selectively locate cationic group on the aperture of the host exterior to form a dicationic dangling host-guest complex. Moreover, introducing a tertiary amine moiety nearby one face of the cluster (surrounded by three naphthalene functionalities) results in formation of an ammonium ion in basic condition. The design and the characterization of the above system will be discussed.

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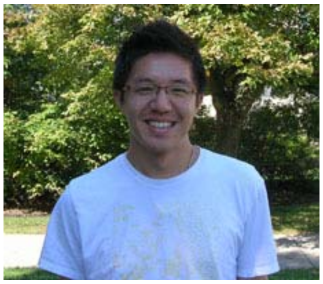
Biography



KaKing Yan received his B.S. in chemistry from State University of New York at Binghamton in 2006 working with Prof. David C. Doetschman and his Ph.D from Iowa State University in 2013 under the direction of Prof. Aaron D. Sadow. He is currently doing his postdoctoral work with Profs. F. Dean Toste, Robert G. Bergman, Kenneth N. Raymond at University of California, Berkeley.

Regioselective C-C Bond Activation of Benzocyclobutenones & Application in Natural Product Synthesis

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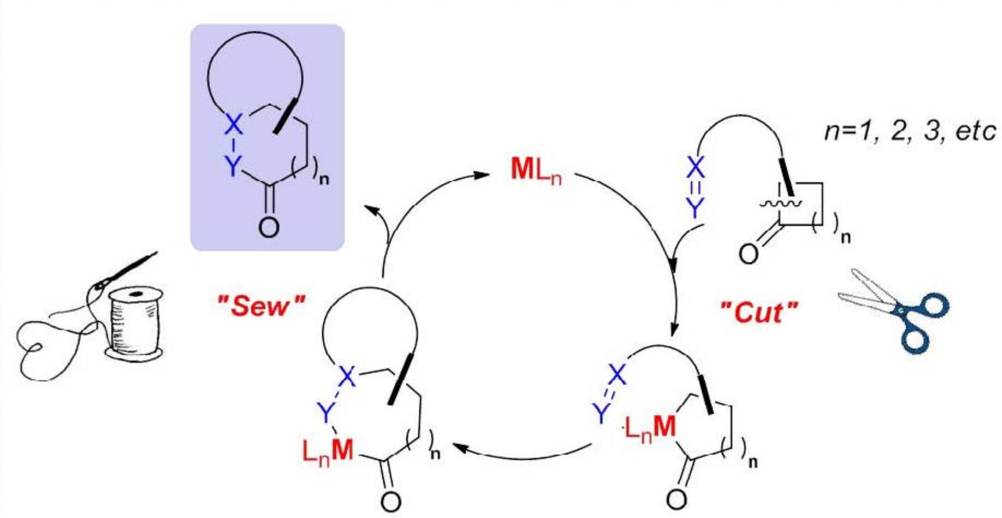
Fused and spirocyclic rings play a pivotal role in both natural products and biologically active molecules. However, efficiency in constructing these structural motifs is always considered as a huge challenge and, once improved, will generate significant impact on organic synthesis. Here, I will describe a non-conventional but efficient strategy to access structurally complex fused/spirocyclic ring systems through transition-metal-catalyzed C-C bond activation. Through systematic investigation, we have developed several protocols to regioselectively activate C-C bond of benzocyclobutenones and access several types ring structures based on a unified activation logic. It is anticipated that a great diversity of scaffolds that are difficult to access by conventional methods would be afforded using this approach. Diterpene natural product, cycloinumakiol, was synthesized in 9 steps and 15% overall yield using our C-C activation strategy, demonstrating the practicality of this methodology in complex molecule synthesis.



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Biography

Tao Xu received his B.Sc. with honor from Dalian University of Technology and completed his Ph.D. degree in chemistry at Peking University under the supervision of Professor Zhen Yang. Upon graduation, he shifted his research topic from total synthesis to transition-metal-catalyzed inert bond activation and worked with Professor Guangbin Dong at University of Texas at Austin as a postdoctoral researcher. There he first developed a regioselective Rh^I-catalyzed C-C bond activation protocol, which would rapidly access fused /spirocyclic ring structures and ultimately applied in natural product synthesis.

Radical ligands with chirality

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Ligands play a very important role in metal-mediated or catalyzed reactions. Not only reactivity, but also selectivity can be controlled by ligands. Traditionally, ligands could be classified by neutral ligands, anionic ligands, cationic ligands. Radical ligands are ignored because radicals are usually regarded as be unstable and unselective. The remarkable photoredox properties of ruthenium and iridium polypyridyl complexes to realize a variety of photocatalytic transformations upon irradiation with visible light inspired us to study the ligand effect.[1] The spectroscopy of these ligands shows radical can exist on the ligands. Chirality is widely exist in nature. An ideal way to prepare chiral compounds is using catalytic asymmetric reactions with chiral catalysis. Our research is based on the theory of chiral counter ions and chiral-at-metal to design and synthesize novel visible light chiral photocatalysis with transition metals and radical ligands. Developing new asymmetric organic transformations and constructing the core of some natural products and drugs by using these photocatalysis. Try to build up a new catalyst pool, discover the relationship between substrates and catalysts, create catalytic models.

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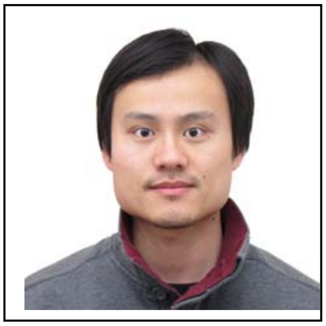

Zhan Lu was born in 1981 in the Zhejiang Province. He received a BSc (2003) and a Ph.D. degree (2008) under the supervisor of Professor Shengming Ma in Chemistry from Zhejiang University. After postdoctoral research with Professor Shannon S. Stahl and Professor Tehshik P. Yoon at University of Wisconsin-Madison, he returned to Zhejiang University in 2013 and joined the chemistry faculty. Currently his research interests focus on radical chemistry, transition-metal catalysis, new methodologies for asymmetric synthesis.

Ab initio calculations of atomic configurations, electronic structures and charge transports in colloidal nanocrystals

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We will present some recent progresses in ab initio calculations of colloidal nanocrystals. This includes the surface passivation of PbS quantum dot [1]; the passivation and growth model of Pt quantum dot [2]; the exciton binding energy in a CdSe/CdTe nanowire [3]; the charge transfer between connected quantum dots [4] and between one CdSe quantum dot and an attached ferrocene molecule [5]. The ab initio calculation has been used to study the atomic structure of PbS quantum dot passivation by oleic acid. It was found that the OH group plays an important role in the surface passivation. This has been confirmed by subsequent experimental observations. The ligand passivation on the surface of Pt nanocrystal also plays an important role in the growth of the nanocrystal, not by the conventional thermodynamic mechanism, but by a kinetic process. While the surface energy of the (111) surface is less than that of (001) surface, the growth will continue on the (111) surface until it disappears. We explain this by the ligand mobility on the (111) surface, which allows it to continue to grow, while the ligand on the (001) surface is immobile, which blocks the surface growth. The self-consistent calculation is used to study the charge transfer exciton in a CdSe/CdTe nanowire. It is found that there is a large exciton binding energy in such a nanowire. Finally, Marcus theory is used to calculate the carrier hopping rate between two connected quantum dots, and one CdS/CdSe core/shell quantum rod and an attached ferrocene molecule. The calculated rate is compared with the experiment. It is found that a the hole transfers directly from the center of the quantum rod core to the ferrocene molecule without the help of any surface intermediate state. We will discuss the general applicabilities and the challenges of using the ab initio calculations to study the atomic and electronic structures of nanocrystals.

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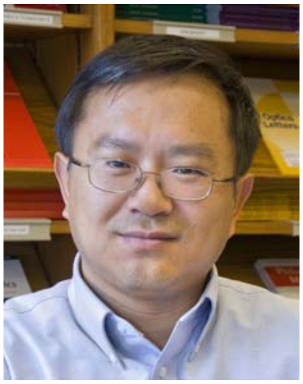

Lin-Wang Wang is a senior staff scientist in Lawrence Berkeley National Laboratory. He is an expert in first-principles simulations of materials and methodology developments. He received his Ph.D in physics from Cornell University in 1991, has authored about 240 peer reviewed papers. His research interest include: methodology developments for large scale electronic structure calculations; non-adiabatic molecular dynamics; million atom quantum mechanical device simulations; study of optical and electronic properties of nanostructures; impurity and defect energy level calculations and semiconductor alloys. He has developed several software packages: folded spectrum method (Escan); linear combination of bulk bands method (LCBB); plane wave pseudopotential method (PEtot), and quantum transport method (PEtot_trans).

Computational Studies of Cycloaddition Reactions: Mechanisms, Reactivities and Selectivities

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A preeminent goal of organic synthesis is to achieve structural complexity with functional value in an atom-, step-, and time-economical fashion. Cycloadditions, as exemplified by Diels-Alder reaction, represent uniquely powerful processes to achieve this goal. This presentation will cover our recent computational studies on the mechanisms, reactivities and selectivities of the transition-metal-catalyzed and organocatalyzed cycloadditions, particularly on the (5+2) cycloadditions with vinylcyclopropanes (VCPs) and (3^++2) cycloadditions with 1,3-monopoles. With density functional theory (DFT) calculations, we have shown the distinctive mechanistic changes when different transition metals, rhodium, ruthenium[1], and nickel[2], are applied in the metal-catalyzed (5+2) cycloadditions with VCPs. On the Rh-mediated (5+2) cycloadditions with allenes, we found a unique allene-catalyst rhodacycle that irreversibly sequesters the rhodium catalyst[3]. This hidden catalyst-poisoning pathway explains a general and counterintuitive phenomenon in Rh-catalyzed intermolecular cycloadditions with allenes, that the more sterically encumbering substrates produce higher yields for the desired cycloadditions. In the study of organocatalyzed (3^++2) cycloadditions, we found that 1,3-monpoles, a type of reactive species that has been discovered decades ago but received little attention, play vital roles in a number of important organocatalyzed transformations. These intermediates are much more reactive than their 1,3-dipolar counterparts, and can facilitate the organocatalyzed metathesis reactions[4], provide high reactivities and selectivities in the Brønsted acid-catalyzed cycloadditions[5], and undergo stereospecific C-H functionalizations[6].

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Biography

Xin Hong is a postdoctoral scholar in the Houk group of Department of Chemistry and Biochemistry of UCLA. He received his B. S. with honors (2010) at USTC, working with Prof. Yao Fu, and Ph. D. (2014) at UCLA, working with Prof. K. N. Houk in the area of computational organic chemistry. Xin's research focuses on understanding reaction mechanism at molecular level through electronic structure calculations, and elucidating fundamental principles and controlling factors for the reactivity and selectivity of important chemical transformations. As a prominent research associate in the Houk group, Xin has led successful collaborations with a number of world-renowned experimentalists, including Prof. Wender and Prof. Trost from Stanford University, Prof. Baran from The Scripps Research Institute, and many others. These productive collaborations have provided mechanistic insights for many important chemical transformations, and led to a series of prestigious publications. Xin's achievements have been awarded with the Excellence in Second Year Academics and Research, Christopher Foote Fellowship and Saul and Sylvia Winstein Dissertation Award, by the Department of Chemistry and Biochemistry of UCLA.

Low Dimensional Semiconductor Nanocrystals for Efficient Charge Separation and Implications for Solar Energy Conversion

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Low dimensional quantum confined semiconductor nanocrystals have been widely investigated as light harvesting and charge separation components in advanced photovoltaic and photocatalytic devices. The efficiency of these semiconductor nanocrystal-based devices depends on many processes, including light harvesting, carrier relaxation, charge separation and charge recombination. The competition between forward and backward reactions determines the overall solar light-to-electricity or fuel conversion efficiency. Compared with single component nanocrystals, semiconductor nanoheterostructures, combining two or more materials, offer additional opportunities to control their charge separation properties by tailoring their compositions and dimensions through wavefunction engineering. In a series of recent studies, using time-resolved spectroscopy, we show that the efficiency of single and multiple exciton dissoication from semiconductor nanocrystals can be effectively controlled by their dimensions and compositions. [1-4] With (quasi)-type II band alignment, forward reactions (charge separation and hole filling) can be facilitated, while the backward recombination (charge recombination and exciton-exciton annihilation) can be simultaneously retarded. [5] With asymmetric dot/rod nano-heterostructures where both electron and hole are exposed to charge collection environment, we show near-unity quantum yield of redox mediator (methylviologen radical) generation. When coupled with Hydrogen evolution (Pt) or CO_2 fixation catalysts (formate dehydrogenase), these nanorods lead to efficient and stable solar-to-fuel (H_2 or HCOOH) conversion performances. [6-7]

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Biography

Haiming Zhu received his B.S. degree in Chemistry from the University of Science and Technology of China in 2008 and PhD from Emory University in 2014. During his PhD in Tianquan Lian’s group, he studied the carrier dynamics and charge transfer properties of quantum confined semiconductor nanocrystals and their applications in solar energy conversion through transient absorption spectroscopy. He is currently a postdoc fellow in Columbia University in the City of New York. His research now focuses on photophysics of low dimensional semiconductor nanomaterial and their heterostructure at single particle level by combining ultrafast spectroscopy techniques with high spatial resolution microscopes.

Solid State NMR for Characterizing Metal-organic Frameworks

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Metal-organic frameworks (MOFs) are an important class of porous materials that are endowed with large surface areas, controllable pore sizes and tunable surface chemistry. These desirable properties make them excellent candidates for gas adsorption applications, e.g. to capture CO_2 and reduce greenhouse gas emissions. Recent developments of MOFs are leading to breakthroughs in gas adsorption performance. Along with fast evolution of new MOF materials, solid-state nuclear magnetic resonance (NMR) plays a crucial role in understanding the physical basis and guiding the material and process design. It is one of the most powerful characterization techniques for analyzing chemical structures, studying molecular dynamics, and microscopic morphologies. The presentation will demonstrate several examples of the unique applications of solid-state NMR for characterizing MOFs, including MOFs with multivariate linkers [1], CO_2 dynamics in MOFs [2,3], and a miniaturized NMR for fast surface area screening [4].

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Biography

Dr. Kong graduated with B.S. from University of Science and Technology of China in 2005 and got his Ph.D. in Iowa State University in 2010. In 2010-2013, He spent 3 years as a postdoctoral fellow in University of California Berkeley and Lawrence Berkeley National Laboratory, following Professor Jeffrey Reimer and Professor Omar Yaghi. Then, he worked as a senior engineer in the Materials Lab of HGST Inc in 2013-2014. In Sept. 2014, he joined the faculty of the Chemistry Department in Zhejiang University. His research interest is solid-state NMR techniques and their applications in materials science, e.g. porous materials, polymer composites etc. His work has been published in *Science*, *Journal of the American Chemical Society*, *Angewandte Chemie*, *International Edition* and so on. He served as a committee member of the Oversea Chinese Magnetic Resonance Society.

Atomic-Resolution Spectroscopic Imaging and In Situ Environmental Study of Bimetallic Nanocatalysts

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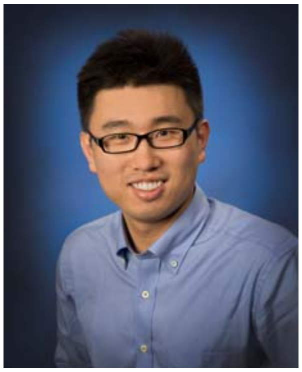
Bimetallic nanoparticles are promising candidates for electro- and heterogeneous catalysis because their catalytic activity is frequently superior to their monometallic counterparts. However, the additional degree of freedom introduces a new complexity into the mechanism because the distribution of the two metals may vary during reaction. For example, preferential adsorption of reactive molecules can induce segregation of one component, structural changes, and element-specific phase transformations. Uncovering the chemistry, structure, and degradation pathways of materials under catalytic conditions is of fundamental importance for establishing structure-property relationships and for the design of new catalytic materials. Aberration-corrected scanning transmission electron microscopy (STEM), in combination with electron energy loss spectroscopy (EELS), is exquisitely poised for studying structural, compositional, and electronic properties of nanocatalysts. The enlarged numerical aperture coupled with the use of a cold-field-emission gun allows for the acquisition of 2-D compositional and bonding maps of both bulk and nanostructured materials at atomic resolution. Additionally, the development and inclusion of differentially-pumped gas cells inside a transmission electron microscope (TEM) permits the visualization of solid-gas chemical reactions *in situ*. Imaging atomic-scale reaction dynamics and the acquisition of spectroscopic fingerprints allows us to reveal reaction pathways that cannot be resolved by any other approach. Here, I will provide background on our techniques, including STEM, EELS, electron tomography, and *in situ* environmental methods, and I will show how the surface and internal structures of Pt-transition metal bimetallic nanocatalysts reconstruct in response to annealing, acid leaching, operational aging, gas oxidation, and reduction.

Biography

Huolin Xin is a staff scientist and a principle investigator in the Center for Functional Nanomaterials at Brookhaven National Laboratory. His primary field of expertise lies in developing novel 3-D, atomic-resolution, and in situ spectroscopic and imaging tools to probe the structural, chemical, and bonding changes of energy materials during chemical reactions or under external stimuli. In 2008, 2010, 2011, and 2012, he received Distinguished Scholar Award, Castaing Award, and Presidential Scholar Award from two



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Towards Solution-processed and High-performance Optoelectronic Devices

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Solution-processed optoelectronic devices, such as solar cells and light-emitting diodes (LEDs) are attractive owning to the advantages of fabricating low-cost and large-area devices and the compatibility with light-weight and flexible plastic substrates.

In this talk, I will present our recent progresses on solution-processed optoelectronic devices based on two classes of materials, quantum dots and hybrid perovskites.[1-2] Our activities on developing solution-processed oxide interfacial materials will also be reviewed.[3-5] With innovations on device structure, our research on quantum-dot LEDs leads to the best-performing solution-processed red LEDs to date with color-saturated emission, record efficiency, low efficiency roll-off, sub-bandgap turn-on voltage, excellent reproducibility, and outstanding operational stability, whose overall performance is comparable to state-of-art OLEDs from vacuum deposition. We also demonstrate highly efficient, stable and reproducible planar heterojunction perovskite solar cells with impressive power-conversion efficiencies (PCEs) up to 15.9%. The superior device performance is achieved by optimizing film processing of the active layers and interfacial engineering to improve cathode contacts. These results highlight that advances of material chemistry to create new building-blocks and device engineering to integrate the functional materials in a rational manner are critical for the development of high-performance and solution-processed optoelectronic devices.

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Biography

Education and Work Experience

1998 – 2002	Peking University, Beijing, China B.Sc. in Chemistry.
2002 – 2006	University of Sussex, Brighton, UK D.Phil in Chemistry (with Prof. Sir Harold Kroto)
2006 – 2007	Cavendish Lab, University of Cambridge, UK Research Associate (with Prof. Neil Greenham)
2007– present	State Key Lab of Silicon Materials, Zhejiang University, China Associate Professor

Dr. Yizheng Jin is interested in materials chemistry, device processing and device physics for solution-processed optoelectronic devices. His research has led to over 40 publications with a citation number of >1,400.

Conjugated Polymers in Solid State: Preparation, Characterization, and Conduction

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Conjugated polymers have attracted great interests for their electronic and optical properties. Poly(diiododiacetylene), or PIDA, is a conjugated polymer containing a poly(diacetylene) backbone and only iodine atom substituents [1], as shown in Figure 1. The monomer molecules of diiodobutadiyne can be aligned in a template formed by self-assembled ureas or oxalamides, and polymerize within the template if their alignment favors the head-to-tail 1,4-polymerization [2]. After the template has been removed, PIDA forms highly-oriented nanofibers with diameters of 10-50 nm [3]. Treating PIDA fibers with Lewis bases such as pyrrolidine or pyridine leads to elimination of iodine content from the polymer. The remaining polymer backbones cross link to form carbon network within the nanofibers, providing a new method to produce carbon/graphitic nanomaterials at room temperature under very mild conditions [4].

Research in the second part focuses on solid-state synthesis of conjugated polymers and oligomers with designed functionalities on Au electrodes [5,6]. Using stepwise Cu(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition, a series of new all-aromatic conjugated polymers (oligomers) have been synthesized on Au electrodes with controlled chain lengths. The length-dependent conduction measurement of these polymers/oligomers reveals a transition in direct current (DC) transport mechanism from tunneling to hopping with increased chain length [7]. In addition, a variety of donor-acceptor block copolymers on Au electrodes have been developed using step imine condensation. The electrical measurement shows that electron flow through the polymer chain is enabled in one direction but suppressed in the other [8]. This diode-like behavior suggests that these materials serve as important candidates for nanoscale electrical components.

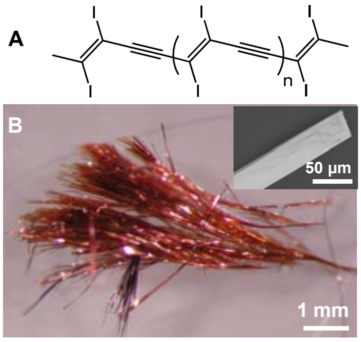

Figure 1. A) PIDA structure. B) Morphology of PIDA fibers.

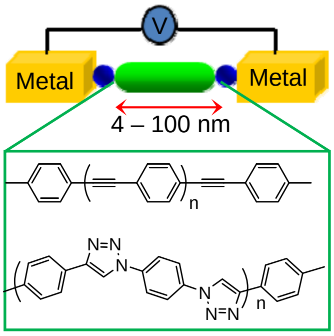

Figure 2. Schematic representation of a molecular junction.

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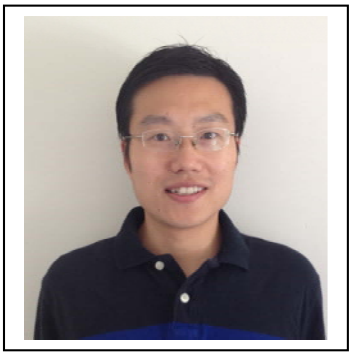
Biography



Dr. Liang Luo received his BS degree in Chemistry and MS degree in Polymer Science from Nankai University. In 2009, he received his Ph. D. in Chemistry from State University of New York at Stony Brook, working on conjugated polymer synthesis, characterization, and preparation. His postdoctoral training in Department of Chemical Engineering and Materials Science at the University of Minnesota focused on designing new conjugated molecular wires for conduction studies and molecular electronics applications. He is now a Research Investigator at Bristol-Myers Squibb Company, USA, and his current responsibilities include molecular properties study and enabling formulations development of drug candidates in support of drug discovery programs. His research interests focus on specific aspects of drug delivery, especially on developing novel polymer materials for controlled release of drug substances. As part of scientific community service, he currently serves as an Executive Committee member in Sino-American Pharmaceutical Professionals Association.

Pd-Catalyzed Direct Functionalization of Unactivated $C(sp^3)$–H Bonds

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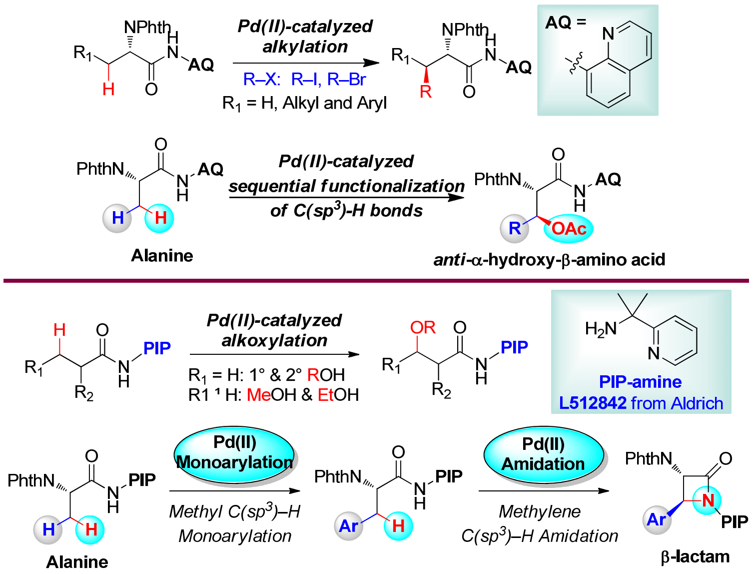
In recent years, transition-metal-catalyzed direct functionalization of unactivated C–H bonds has emerged as an attractive alternative to traditional cross-coupling reactions due to the minimization of stoichiometric metallic waste and the avoidance of multi-step sequences to prepare the starting materials. Compared to the significant progress made with the functionalization of $C(sp^2)$–H bonds of arenes and heteroarenes, general strategies for the functionalization of unactivated $C(sp^3)$–H bonds, especially methylene $C(sp^3)$–H bonds, remain relatively rare. Our group has focused on Pd(II)-catalyzed functionalization of unactivated $C(sp^3)$–H bonds and their application in the total synthesis and late-stage functionalization of bioacivated molecules.



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Biography

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2010.05 - present: PI, Zhejiang University
2007.8 – 2010.4: Research Associate, The Scripps Research Institute
2006.10 – 2007.7: Postdoctoral Fellow, University of California, San Diego
2001.9 – 2006.7: Ph.D., Shanghai Institute of Organic Chemistry, CAS
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Development of Anti-Tumor Vaccines Using Mucin Glycopeptides

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The membrane-bound MUC1 glycoprotein is expressed on normal glandular epithelium of many tissues. Its N-terminal extracellular domain contains highly conserved variable number tandem repeats (VNTR) of 20 amino acid residues: HGVTSAPDTRPAPGSTAPPA, with modification by complex *O*-linked glycans on serine and threonine sites. Due to the changes of glycosyltransferase expression in malignant cells, glycosylation on the VNTR is dramatically altered in human carcinomas. The glycans are characteristically truncated and prematurely sialylated to form tumor-associated saccharide antigens, such as Tn, T, STn and ST antigens. The underglycosylation also exposes the core peptide epitopes. These tumor-associated saccharides together with the peptide backbone epitopes make MUC1 an important target for cancer immunotherapy. However, these endogenous glycopeptides are very low immunogenic and additional stimulation is required to induce strong immune responses to overcome the natural immune tolerance. To this end, several strategies have been developed in our research to booster the immune responses against MUC1 glycopeptides.

The full length MUC1 VNTR sequence with glycosylation on threonine-9 and serine-15 was covalently conjugated to bovine serum albumin (BSA), and subsequently administered to mice for vaccination.[1] Immunological evaluation indicated that the glycosylation patterns and sites could influence the immune responses in the matter of antibodies level and antibodies binding to tumor cells. To avoid the interference from the peptide epitopes included in carrier protein, we simplified the vaccine structures and synthesized some two-component vaccines using T-cell epitope peptides or toll-like receptor ligand lipopeptide.[2,3] These vaccines induced very strong immune responses in mice without any external adjuvants. Also we combined the MUC1 glycopeptides, T-cell epitope peptides and lipopeptide to construct three-component vaccines.[4] More recently, we developed multivalent vaccines using lipopeptide or gold nanoparticles as scaffolds.[5,6] These antisera induced by these vaccines exhibited strong binding to tumor cells, and some of the antisera could induce strong complement dependent cytotoxicity. We further evaluated the specific binding of antisera to glycopeptides library by microarray analysis.

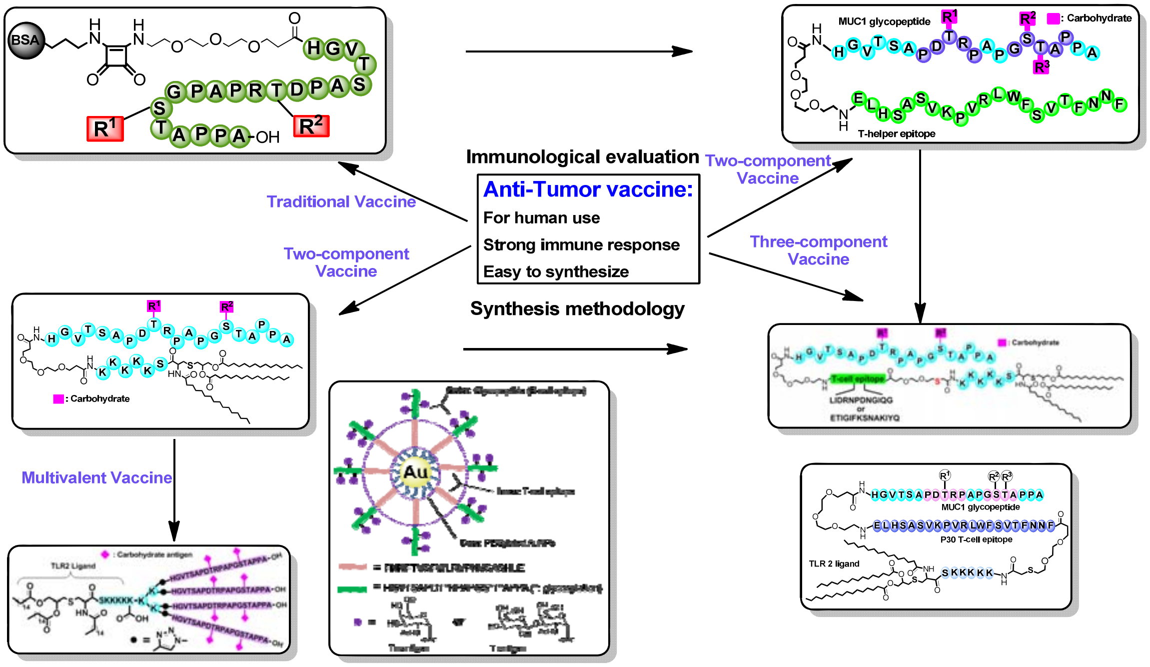

Figure 1. Strategies for development of glycopeptides anti-tumor vaccines.

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Biography

Dr. Hui Cai was born on 1st. Dec. 1981 in Hunan province. From 2001 to 2005, he majored in chemistry at the college of chemistry and chemical engineering in Hunan University for his bachelor degree. From 2005-2011, he executed his Ph.D. research at the department of chemistry in Tsinghua University under the supervision of Prof. Dr. Yan-Mei Li. Then he was employed as a postdoctoral researcher at Prof. Li's group for one year. Since 2012, Dr. Hui Cai is working at Leibniz institute for analytical science in Germany with a postdoctoral research fellowship from Alexander von Humboldt Foundation. His research is focus on the development of anti-tumor vaccines using mucin glycopeptides.

Studies toward the Total Synthesis of Steenkrotins A and B

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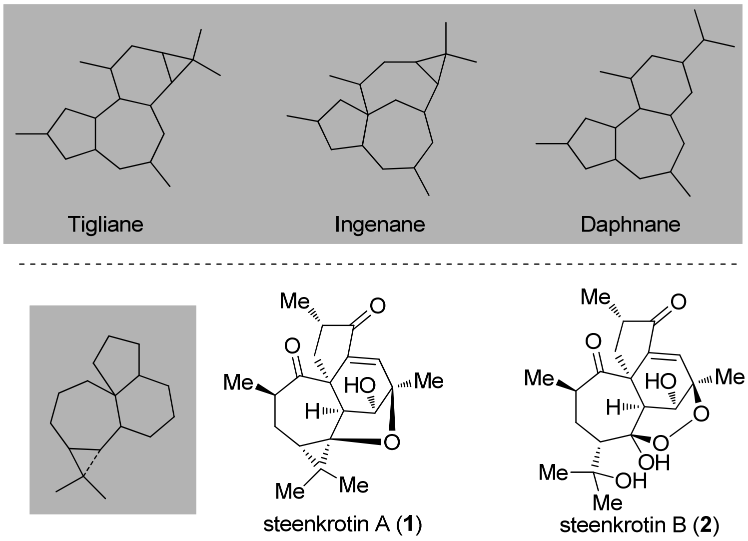
Croton steenkampianus Gerstner (Euphorbiaceae), commonly known as “Marsh Fever-berry” and “Tonga Croton”, is a shrub or tree endemic to restricted areas of central Africa and eastern parts of southern Africa. Various medicinal uses of the genus *Croton* are reported in countries all over the world, and many species are used to treat bleeding, bleeding gums, chest complaints, coughs, fever, indigestion, malaria, and rheumatism. In 2008, Hussein and co-workers isolated two novel natural diterpenoids from the ethanol extract of leaves of *C. steenkampianus*, which they subsequently named steenkrotins A and B (Scheme 1).[1] Steenkrotin A (**1**) contains a unique [3,5,5,6,7]pentacyclic skeleton while steenkrotin B (**2**) features a unusual [5,6,6,7]tetracyclic framework including an intriguing endoperoxide ring, both of them consist of six contiguous stereogenic centers. The highly complicated and congested structures and potentially important biological activities have rendered steenkrotins A and B as attractive targets for synthetic studies. In this presentation, we will disclose our recent progress towards the total synthesis of **1** and **2**.



Scheme 1. Structures of steenkrotins A and B

†S.P and J.X. contributed equally to this work.

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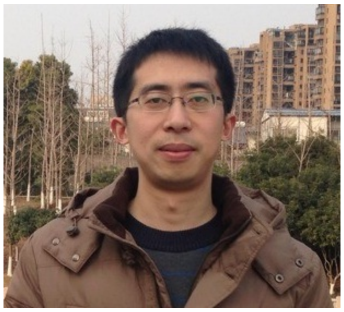

丁寒锋

特聘研究员，博士生导师

Dr. Hanfeng Ding

Education:

2008-2011 Research Fellow, Institute of Chemical & Engineering Sciences (ICES), A*STAR, Singapore

2003-2008 Ph.D. in Organic Chemistry, Zhejiang University

1999-2003 B.S. in Chemistry, Zhejiang University

Research Interests:

- Total synthesis of structurally complex and bioactive natural products
- Development of new synthetic methodologies inspired by natural product synthesis

Recent publications:

1. "Stereoselective Total Synthesis and Structural Elucidation of (–)-Indoxamycins A-F" C. He, C. Zhu, B. Wang, H. Ding.* *Chem. Eur. J.* **2014**, *in press*.
2. "Diastereoselective Total Synthesis of Salvileucalin C" C. Fu, Y. Zhang, J. Xuan, C. Zhu, B. Wang, H. Ding.* *Org. Lett.* **2014**, *16*, 3376–3379. (*"Most Read Article"* of June 2014)
3. "Synthetic Strategies toward the Indoxamycin Family" C. He, C. Zhu, H. Ding.* *Synlett* **2014**, 1487–1493. (Invited *Synpacts* Article)
4. "Divergent Total Synthesis of Indoxamycins A, C, and F" C. He, C. Zhu, Z. Dai, C.-C. Tseng, H. Ding.* *Angew. Chem. Int. Ed.* **2013**, *52*, 13256–13260. [Highlighted by *RSC "Chemistry World"*; Highlighted by *"Organic Chemistry Portal"* (April 21, 2014); Featured in *Synfacts* (**2014**, 0003); Featured in *Chin. J. Org. Chem.* (**2014**, *34*, 230)]

Identification of Mammalian Nuclear RNA *N*^{6}-Adenosine Methylation Complex

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Discovered in the 1970s, m^{6}A is the most prevalent internal modification in polyadenylated mRNAs and long non-coding RNAs in higher eukaryotes, although it also exists in ribosomal RNA, transfer RNA, small nuclear RNA and so on.[1] m^{6}A is widely conserved among eukaryotic species that range from yeast, plants, flies to mammals, as well as among viral RNAs. But, the biological functions of m^{6}A modification are largely unknown mostly because the methyltransferase complex itself remains a mystery. In this talk, I will introduce how the human nuclear RNA m^{6}A methyltransferase core complex was for the first time biochemically identified and characterized.[2] The direct RNA binding sites and target genes of the methyltransferase complex were revealed in a transcriptome-wide manner by high-throughput sequencing methods.

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Biography

I got my BSc degree in 2006 from Department of Polymer Science and Engineering from Zhejiang University and got my PhD degree in 2011 under the supervision of Chinese academician Prof Ben Zhong Tang from The Hong Kong University of Science and Technology. I am currently doing my postdoc under Howard Hughes Medical Institute investigator, distinguished professor Chuan He in Chemistry Department at The University of Chicago. I was trained in synthetic chemistry, polymer chemistry, and material chemistry in my PhD study, and studied chemical biology, biochemistry, and nucleic acid (DNA/RNA) biology during my postdoc. In my PhD thesis work, I developed several carbon-carbon triple bond-based polymerization reactions, e.g., homocyclotrimerization of diyne monomers and thiol-yne click polymerization, to make new functional polymers with different dimensionalities and advanced photo-electronic properties. I also had expertise in using small organic fluorescent probes for bio-sensing and trafficking, such as cancer cell targeting and labeling, intracellular pH measurement, protein and nucleic acid quantification, monitoring intracellular processes, and so on. Recently, we have for the first time identified and characterized the human nuclear RNA N6-adenosine (m^{6}A) methyltransferase complex, which catalyzes the m^{6}A methylation on mRNA, non-coding RNA, and other forms of nuclear RNAs. I am now working on elucidating the mechanisms of m^{6}A modification selectivity on the whole transcriptome and the roles of m^{6}A in RNA metabolism.

Designed Synthesis, Modification and Assembly of Nanomaterials for Biomedical Applications

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Nanotechnology has received extraordinary attention recently due to its burgeoning role in biomedical science. The materials composing the nanoparticles produce fascinating and diverse functionalities as a result of their exceptionally small size. Size control, both during synthesis and in particle suspensions, is a *sine qua non* for functionality. This can be accomplished by masking the particle surface with a multitude of different ligands [1, 2]. Ligands are essentially fungible and can be exchanged at various times to confer the desired properties to the particle. This can include protecting the particle from harsh aqueous conditions [3, 4], such as pH extremes, maximizing optical properties for diagnostics or shielding the particle from potentially hostile conditions found in the body. The design of the ligand can have crucial effects on biodistribution as well as evasion of biological defenses. Ligands can even be designed to provide new functionality in response to various environmental stimuli to improve their therapeutic or diagnostic capabilities [5, 6]. Clever combination of different nanoscale materials via ligand-directed self-assembly will lead to the development of multifunctional nano-biomedical platforms for simultaneous targeted delivery, fast diagnosis, and efficient therapy [7-9].

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Biography

Daishun Ling received his PhD (supervisor: Prof. Taeghwan Hyeon) in the School of Chemical and Biological Engineering of Seoul National University in 2013. Currently, he is working as a senior researcher at the Center for Nanoparticle Research, Institute for Basic Science. Recently, he focuses on the synthesis of inorganic nanoparticles, organic/inorganic hybrid materials, and the design of nanoparticle surface ligands for the development of novel nanoplatforms for medical diagnosis and therapy. He received Chinese Government Award for Outstanding Students Abroad and Outstanding Young Scholar Award (Nanotoxicology) in 2012.

Directed Synthesis of Boron-Based Cluster Anions

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Boron-based cage anions $[B_{12}R_{12}]^{2-}$ and $[CB_{11}R_{12}]^{-}$ are inorganic/organic hybrid molecules which possess unique steric and electronic properties that differentiate them from common metal complexes and organic molecules (**Figure 1**) [1,2]. Furthermore, they are very stable and exhibit low toxicity. The utility of boron cage compounds has been demonstrated in the areas of stereoselective synthesis, fluorescence as well as phosphoresence applications, materials science and biological chemistry. [3-7]

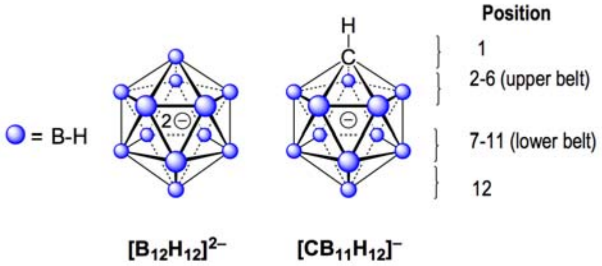

Figure 1. Icosahedral boron-based cluster anions.

Current synthetic limitations have so far prevented the widespread use of $[B_{12}R_{12}]^{2-}$ and $[CB_{11}R_{12}]^{-}$ anions. Our goal is to develop innovative and convenient methods for the selective synthesis of functionalized borane and carborane cage compounds.

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Biography

2013 - present: Research Professor at the Department of Chemistry of Zhejiang University

2010 - 2013: Postdoctoral fellow at Yale University (Advisor: Prof Jonathan A. Ellman)

2007 - 2008: Research associate at the University of California, Riverside (Advisor: Prof. Christopher A. Reed)

2005 - 2010: PhD student at the University of Zurich (Advisor: Prof. Jay S. Siegel)

Electrocatalytic Reduction of CO_2 to Formate and Syngas Using Molecular Catalysts

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The reduction of CO_2 to high-energy, value-added chemical intermediates such as formic acid/formate and CO is a key step in utilizing CO_2 for production of solar fuels and useful chemicals. To accomplish such transformations, iridium and ruthenium catalysts have been developed to catalyze the $2e^-$ reduction of CO_2 to formate and syngas (CO/H_2 mixtures).

Ir PCP-type pincer catalysts have been developed to reduce CO_2 to formate electrocatalytically in non-aqueous media [1] and in water [2] with high efficiency and selectivity. Formate is the only reduced carbon product, formed in 93% Faradaic yield with no formation of CO. The high selectivity for formate production over H_2 originates from the aqueous stability of Ir dihydride species, the active species for reduction of CO_2. As further pursuit of reducing CO_2 in water, an iridium pincer dihydride catalyst was immobilized on carbon nanotube-coated gas diffusion electrodes (GDEs) by using a non-covalent binding strategy [3]. High turnover numbers (~200,000) and turnover frequencies (~15 s^{-1}) were observed in aqueous solutions saturated in CO_2 with added HCO_3^- enabled by the novel electrode architecture.

Synthesis gas, H_2:CO (syngas), is a key feedstock for the chemical industry. Currently it is mainly derived from fossil sources. We reported a simple electrocatalytic procedure for the reduction of water saturated in CO_2 with added bicarbonate to give adjustable H_2:CO syngas ratios with the use of a single Ru(II) polypyridyl carbene catalyst in both the cathode and anode compartments [4]. At the cathode the syngas ratio can be adjusted between 4:1 and 1:2 by controlling either the electrolysis potential or the solution pH. The same catalyst at the anode also catalyzes water oxidation to O_2 which releases protons for water/CO_2 reduction at the cathode. The electrolysis cell for making syngas is simple, robust, and relatively energy efficient with overall energy efficiencies of ~50%.

The molecular catalysts for electrochemical reduction of CO_2 have been developed to generate formate and syngas in aqueous phase. These electrocatalysts are important components for photoelectrochemical CO_2 reduction to solar fuels, and integration of these catalysts into Dye Sensitized Photoelectrosynthesis Cells (DSPEC) in conjugate with molecular chromophores is currently underway.

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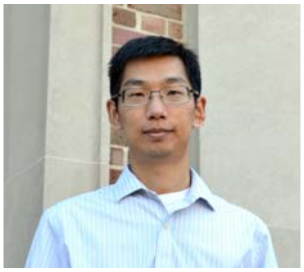
Biography



Dr. Peng Kang received B.S. in Chemistry from University of Science and Technology of China in 2004 and Ph.D. in Chemistry from Stanford University in 2010. Currently he is a postdoctoral research associate under joint supervision by Prof. Maurice Brookhart and Prof. Thomas J. Meyer in the Chemistry Department of UNC-Chapel Hill. His research focuses on reduction of carbon dioxide to fuels and chemicals powered by renewable energy, supported by UNC Energy Frontier Research Center: Solar Fuels. He has developed several molecular catalysts that can produce formate/formic acid and synthesis gas (hydrogen/carbon monoxide mixtures) from carbon dioxide. He also innovated flow electrolysis reactors to integrate the above mentioned molecular catalysts. With 10+ publications and patents, his research have significantly furthered the understanding of employing carbon dioxide as a sustainable feedstock for the production of chemicals and fuels, and have promoted translation of fundamental laboratory discoveries to industry and marketplace, closing the gap between basic and applied research. Dr. Kang also served as CO_2 reduction team coordinator in the Energy Frontier Research Center of UNC, and promoted interactions among scientists from different fields.

Catalytic materials for energy conversion and storage

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My research interests focus on fundamental understanding of catalytic processes and development of highly active (or selective) and durable catalysts for the reactions of industrial importance, especially for energy conversion and storage. I establish a research system that connects fundamental investigation on well-defined extended surfaces (e.g. single crystal surfaces), extrapolation onto nanocrystals with highly controlled shape and size, exploration of interfacial interaction using novel nanocrystal superlattices as platform, and finally design of high performance catalysts in which all the possible beneficial properties from complex functional structures are implemented.

The fundamental understanding of correlationship between materials structure and catalytic properties is the key to design new catalysts with desired properties. The very first step would be understanding the most simplified surface processes using well-defined extended surfaces and computer-powered theoretical simulations. However, the real catalysts used in industrial processes are mainly nanomaterials that take advantage of their high surface-to-volume ratio. It is necessary to confirm that the desirable properties found in simplified cases are actually functioning in the nanomaterials. Therefore, well-defined nanocrystals with exposed surfaces mimicking the simplified surfaces which are used in theoretical studies are highly valuable and appreciated. Besides desired surfaces, the interactions among the components within the catalysts are also important. Because of certain desired metal-oxide interfacial interactions that promote catalysis or introduce synergistic effect, metal catalysts supported on oxide supports are the other class of important catalysts that exploit beneficial interactions. In additional to well-controlled size and shape, the structures rendering the desired interactions are needed to carry out the investigation of interfacial effects. Finally, with all the knowledge learned from theoretical studies and investigation on model materials, I am able to design catalyst that incorporates the beneficial properties in a single nanostructure. For example, nanoframes with a desired Pt3Ni composition, a 3D open structure that is highly accessible to reaction species, (111)-like texture, and beneficial surface segregated Pt-rich Skin structure, achieve a 36-fold enhancement in oxygen reduction reaction activity in comparison to state-of-the-art Pt/C catalysts.

Biography

Dr. Yijin Kang is currently a postdoctoral researcher at Materials Science Division, Argonne National Laboratory. He received B.S. from Fudan University (2005) and Ph.D. from University of Pennsylvania (2012). He had a short industrial research experience as an engineer at Global Research, General Electric. He is well-known expert in nanomaterial synthesis and characterization with 21 articles published on top journals and magazine, including Science, JACS, Angewandte Chemie, and ACS Nano. He received over 1000 citations in just a few years.

Selected publications:

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Tunable Plasmonic Nanostructures Enclosed by High-Index Facets: Converging Plasmonics and Catalysis on the Same Nanoparticle

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Noble metal nanoparticles have been of tremendous interest owing to their intriguing size- and shape-dependent plasmonic and catalytic properties. The combination of tunable plasmon resonances with superior catalytic activities on the same nanoparticle, however, has long been challenging because plasmonics and catalysis require nanoparticles in two drastically different size regimes. While tunable plasmon resonances are a unique feature of sub-wavelength metal nanoparticles, heterogeneous catalysis typically requires the use of sub-5 nm nanoparticles as the catalysts. My group has recently demonstrated that desired plasmonic and catalytic properties can be integrated on the same nanoparticle by controllably creating high-index facets on individual sub-wavelength metallic nanoparticles.[1-6] The capabilities to both nanoengineer high-index facets and fine-tune the plasmon resonances through deliberate particle geometry control allow us to use these nanoparticles for a dual purpose: as substrates for plasmon-enhanced spectroscopies and efficient surface catalysts. Such dual functionality opens up unique opportunities for quantitative study of the intrinsic kinetics and mechanisms of surface-catalyzed reactions with unprecedented sensitivity and detail through time-resolved plasmon-enhanced spectroscopic measurements.

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Biography

Hui Wang was born in Nanjing in 1979. He received his B.S. in Chemistry with honors and M.S. in Analytical Chemistry from Nanjing University in 2001 and 2003, respectively. He was a graduate student working with Professor Naomi J. Halas at Rice University from 2003 to 2007 and received his Ph.D. in Physical Chemistry in January 2008. His Ph.D. work focused on plasmon hybridization in complex metallic nanostructures. As a graduate student, he received Robert A. Welch Foundation Predoctoral Fellowship, Materials Research Society Graduate Student Award Silver Medal, Chinese Government Award for Outstanding Student Abroad, Dissertation Award for Outstanding Research in Physical Sciences from Sigma-Xi Society Rice-Texas Medical Center Chapter, and Honorable Mention Award of IUPAC Prize for Young Chemists. From 2007 to 2010, he was a postdoctoral fellow under the tutelage of the late Professor Paul F. Barbara at the University of Texas at Austin. His postdoctoral work focused on using single-molecule fluorescence spectroscopies to resolve the conformational dynamics of protein-nucleic acid complexes. Since September 2010, he has been a tenure-track Assistant Professor in Department of Chemistry and Biochemistry at University of South Carolina. The theme of his independent research is to use physical chemistry approaches -- specifically spectroscopy, microscopy, and electrochemistry -- to tackle challenging problems in both materials and biological sciences. As an independent PI, he received a National Science Foundation CAREER Award in 2013 and was named a Breakthrough Star by the University of South Carolina System in 2014.

Synthesis of Porous Metalloporphyrinic Frameworks for Heterogeneous Biomimetic Catalysis

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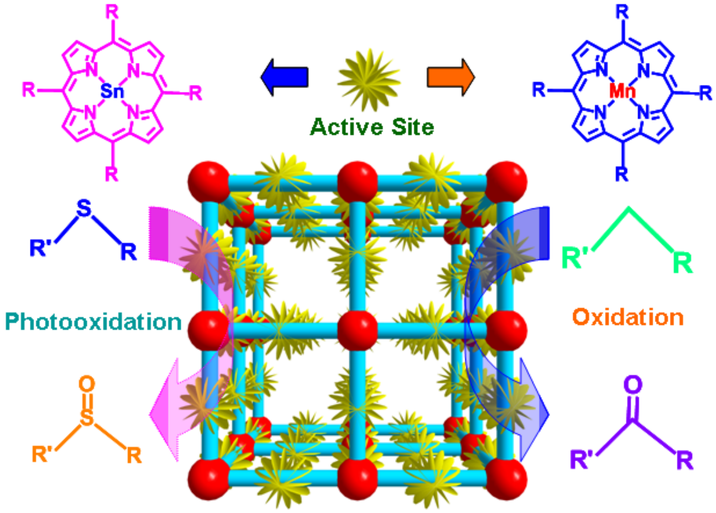
Metalloporphyrins are the active sites in monooxygenases for the highly efficient oxidation of a variety of substrates under mild conditions. The artificial metalloporphyrins have different catalytic activity and sustainability from their counterparts in nature, because these homogeneous metalloporphyrins have heavily suffered from the catalytic deactivation by the suicidal self-oxidation, which have limited their catalytic applications. Inspired by the heme molecules in protein scaffolds which can maintain high efficiency over numerous catalytic cycles, a unique strategy, immobilizing metalloporphyrin moieties into the emerging porous metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs), was therefore developed to introduce their molecular recognitions for the substrates and thus for highly efficient biomimetic catalysis.[1]



The porous structures and framework topologies of the porphyrinic frameworks are dependent on the configurations, coordination donors and porphyrin metal ions of the metalloporphyrin moieties. To improve the functionality of porous porphyrinic frameworks, we have developed the two-step synthesis approach to introduce the functional polyoxometalates (POMs) into POM-porphyrin hybrid materials.[2] To tune the pore structures and the catalytic properties of porphyrinic frameworks, we have designed metalloporphyrin M-H_8OCPP ligands having four *m*-benzenedicarboxylate moieties, and introduced the secondary auxiliary ligands.[3] Incorporation of the biomimetic metalloporphyrins as well as the secondary functional moieties into porous porphyrinic frameworks their catalytic properties and activities toward different reactions, including oxidation of alkylbenzenes, olefins and hexane, and photo-oxygenation of 1,5-dihydroxynaphthalene and sulfides, are highly depending on the porphyrin metal ions and the framework pore structures. We have further revealed that different active sites, including the porphyrin metal ions and the secondary auxiliary sites, in the pores can collaboratively work to enhance the catalytic activities of porphyrinic frameworks by the synergistic effect. Compared with their homogeneous counterparts, the immobilization of metalloporphyrins onto the pore surfaces of porphyrinic frameworks not only prevents their suicidal self-oxidation but also enhances their catalytic activities to activate inert substrate molecules, such as cyclohexane molecules.[4] Moreover, because the bulky substrate molecules have difficulty to access the active sites inside the pores of porphyrinic frameworks, these porous materials demonstrate interesting substrate size-selective catalytic properties. Our studies indicate that porous porphyrinic frameworks are very good platforms to mimic biocatalysts and thus to develop heterogeneous catalysts for a variety of chemical transformations under mild conditions.

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Biography

Chuan-De Wu obtained his Ph.D. in 2003 from Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences under the supervision of Prof. Can-Zhong Lu and Prof. Jin-Shun Huang. After a postdoctoral stint at University of North Carolina at Chapel Hill with Prof. Wenbin Lin, he joined the faculty of Zhejiang University in 2005. His research interest focuses on the synthesis of porous metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) for biomimetic catalysis.

The role of support in heterogeneous catalysis: from ligand effect to redox cycle

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Catalyst supports ensure the dispersion of active materials. They usually offer large surface area and confined geometry, into which active species are anchored and stabilized. However, the actual role of support in catalysis is more complicated than its definition. In Physics, supported particles undergo Winterbottom construction, and thus show different morphology to the free particles. In Chemistry, the support can be active and participates in the catalytic circle. For instance, it is widely accepted that Al_2O_3 and ZrO_2 are active support which could stabilized the active centers on the surface. Therefore, understanding of the role of support is fundamentally important and helps design better performed solid catalysts. In this seminar, two examples are studied with the assistance of carefully designed control experiments and *in situ* studies. The methods used here could serve as potential guideline for future catalysis research.

Suzuki cross-coupling between 1,3-dimethyl-2-chlorobenzene and 2-tolylboronic acid via palladium catalyst is studied first. The reaction involves in three *ortho* groups and chloro-substrate, and can only be performed homogeneously with the help of Buchwald ligands. Here a polyphenylene support, with similar molecular structure of the Buchwald ligands, is developed and shows 83% yields for 20 h reaction at 80 °C and 0.8% catalyst loading[1]. In contrast, carbon and polydivinylbenzene supported palladium (with the same palladium loading and size distribution) do not show any conversions. Thus, the control experiments indicate that π-conjugated polyphenylene support serves as a solid ligand for cross coupling reactions.

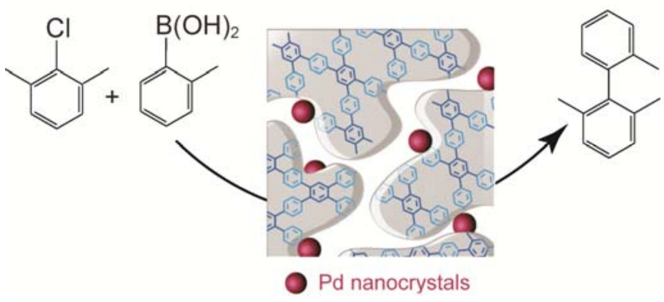

Figure 1: Schematic of the palladium on polyphenylene structure and the cross coupling reaction.

In situ electron paramagnetic resonance (EPR) has been applied to the study of redox properties of CuO–CeO_2 catalysts. The catalysts show potentials in low temperature water-gas shift reaction and CO oxidation. In this study, a quartz plug flow reactor is built inside EPR cavity with is further combined with online gas analysis and mass spectrometry. *In situ* study of the redox kinetics directly reveals the synergy effect of Ce, where Ce participates in the redox cycle.

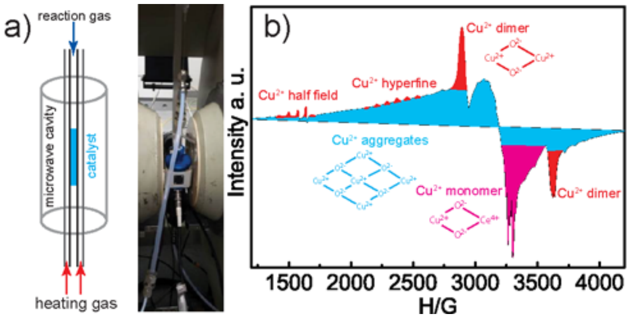

Figure 2: (a) Scheme and digital photo of the quartz plug flow reactor inside the EPR cavity. (b) EPR spectrum of 20wt% $CuO-CeO_2$ at 180 °C. Cu^{2+} monomer, dimer and aggregate are coded in pink, red and blue, respectively.

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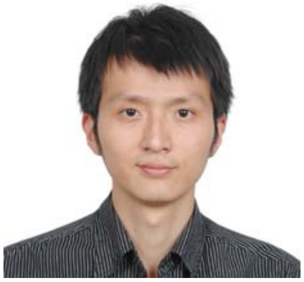

Dr. Feng Wang obtained Ph.D. degree in chemistry in 2012 as a joint degree between Peking University and the Chinese University of Hong Kong, with a focus on colloidal nanomateirals and plasmonic-catalytic mateirals for solar energy harvesting. Currently, he works as Alexander von Humboldt postdoctoral fellow in the group of Professor Ferdi Schüth at the Max-Planck-Institut für Kohlenforschung in Germany. Here he works on support-catalyst interactions, especially the coordination effects and the redox properties of the support materials. He has so far published seven first authored papers, including four *Angewandte Chemie* and two *J. Am. Soc. Chem.*, together with three invited talks. He has established a lab in University of Duisburg-Essen for spray processing of carbon materials, where he is one of the few external researchers accessing the facilities. External funding source is obtained and three PhD students are attracted to his lab.

Design and Fabrication of Hierachically Porous Carbon with a Template-free Method

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Hydrothermal carbonization (HTC) process of saccharides, a traditional and revived technique, is an efficient strategy for the fabrication of sustainable carbon materials. The abundant O-functional groups (-OH, -C=O, -COOH) make as-prepared carbons facile for further modification. However, the absence of porous structure greatly hinders their wide applications. Here, we describe a facile kayexalate (PSS)-assisted HTC method for the controlled synthesis of hierarchical porous carbon materials. The BET surface areas of the materials manufactured by the modified HTC process vary from 20-77 m^2/g. After following treatment at high temperatures, the BET surface areas can reach 1306 m^2/g which is constructed by almost equal micropores and mesopores. The character is preferable in the use of supercapacitor materials, and moreover the rich surface O functional groups provide possibility of pseudo-capacitance. The electric capacitance up to 203 F/g was achieved at 1 A/g in aqueous electrolyte by galvanostatic charge/discharge curves. What's more, the strategy is suitable for both monosaccharides (fructose, glucose) and polysaccharides (sucrose, cellulose).

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Biography

Yong Wang studied chemical engineering at Xiangtan University from 1998 to 2002. He received his Ph.D. degree from Zhejiang University in 2007. After a postdoctoral stay at the Department of Chemistry, Zhejiang University, he joined the Max Planck Institute for Colloids and Interfaces in Potsdam/Germany in 2009. He rejoined Zhejiang University and became a Professor for Chemistry in 2011. His research focuses on carbon nanomaterials and their applications in sustainable chemistry.