天津大学
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1st NUS-TJU PhD Online Workshop
30th Jan 2021

天津大学 - 新加坡国立大学
福州联合学院

1st NUS-TJU PhD Online Workshop

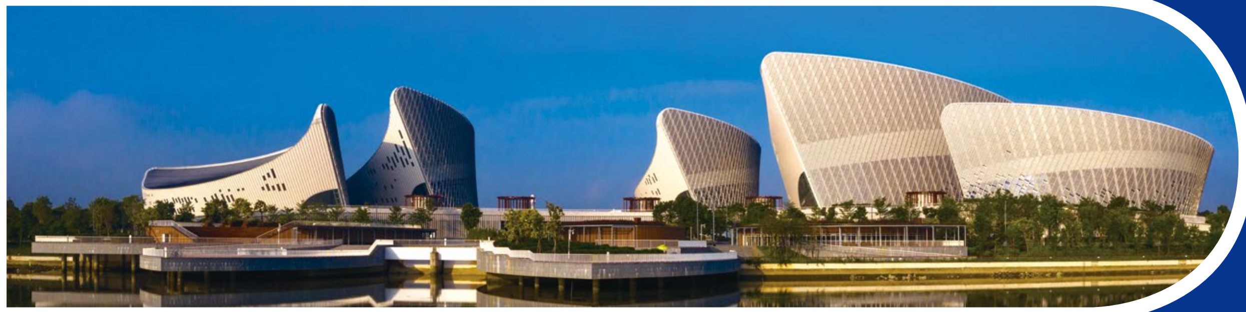
The TJU-NUS Joint Institute in Fuzhou was established as a collaborative project of National University of Singapore, Tianjin University, the People's Government of Fuzhou City and the Education Department of Fujian Province. Fully funded by Fuzhou and located in TJU (Fuzhou) International Campus, the Joint Institute aims to promote research excellence and develop talents in optoelectronics, flexible electronics, advanced chemical manufacturing, energy materials and advanced catalysis. In addition, the Institute also aims to develop technology and support local industry growth in Fuzhou. To promote cutting-edge and collaborative research, three research centers have been established including Emerging Optoelectronics and Flexible Electronics Center, Advanced Manufacturing Center and Energy Materials and Catalysis Center.

Following the signing of agreements on December 1st, 2018, the brand new campus is being constructed in Fuzhou and expected to be fully functional for research and education in middle 2022. Reaching steady state, the Joint Institute will comprise >200 researchers and up to 240 doctoral students working in 30 research groups.

Doctoral students are the core of this trilateral program. By adopting a 1 year (NUS) + 2 years (Fuzhou) + 1 year (NUS) format for their study and research activities, all students will take courses, pass all qualification exams and obtain PhD degree from NUS. In order to encourage active interaction and promote excellence among our students, we have decided to initiate an annual PhD symposium, with the first in its series taking place online in January 2021. We hope that all of you will enjoy this event by sharing your research, learning from your peers and setting a strong culture and tradition in our NUS-TJU Joint Institute in Fuzhou.

2021 Workshop Organizing Committee (Students):
An Chuanbin, Jiang Chonglai, Lin Zhikeng, Liu Zhihe, Wang Meng, Zheng Ying

2021 Workshop Organizing Committee (PIs):
Chen Wei, Geng Yanhou, Xie Jianping, Yan Ning, Zhao Yu



Workshop Schedule

NUS-TJU PhD OnlineWorkshop, 30th Jan 2021

Center 1: Optoelectronics

Symposium Chair: An Chuanbin

		Presenter	**Title**	**Supervisor**
Session Chair: An Chuanbin				
Morning	9:00-9:20	Song Jingting	Wood Based Single Atom Catalysts for Efficient Construction of Substituted Quinolines	Loh Kian Ping
	9:20-9:40	Chen Fangzheng	Metallo-Covalent Organic Frameworks	Loh Kian Ping
	9:40-10:00	Leng Xiaohui	Chemical Vapor Deposition of MoOxSey and Its Electrical Transport Property	Loh Kian Ping
	10:00-10:20	Li Zhuoer	Design and Function of π Electronic Covalent Organic Frameworks	Jiang Donglin
	10:20-10:40	Xie Shuailei	Design and Synthesis of Novel Architectures of Covalent Organic Frameworks	Jiang Donglin
	10:40-11:00: Break			
	Session Chair: An Chuanbin			
	11:00-11:20	Yang Hao	Designed Synthesis of Novel Covalent Organic Frameworks	Jiang Donglin
	11:20-11:40	Pu Guiqiang	Development of Novel NIR Organic Dyes with AIE Properties for Sensitizing NIR-II Luminescence of Lanthanides Doped Nanocrystals	Li Zhen & Liu Xiaogang
	11:40-12:00	Zhao Yao	The Derivatives of Triphenylamine with Room Temperature Phosphorescence	Li Zhen & Wu Jishan
	12:00-12:20	Wang Zao	Tailoring Crystal Facets of Different Catalysts to Enhance Photocatalytic Activity for Hydrogen Evolution	Li Zhen & Wu Jishan
Lunch Break				

		Presenter	Title	Supervisor
Session Chair: An Chuanbin				
Sym2	14:00-14:20	An Chuanbin	Synthesis and Characterization of Multiblock Stretchable Polymer Semiconductors Based on PBTTT	Geng Yanhou & Chi Chunyan
	14:20-14:40	Shao Bo	π-Conjugated Molecules with Quinoidal Structures: Synthesis, Properties and Applications	Geng Yanhou & Chi Chunyan
	14:40-15:00	He Yu	π-Conjugated Materials with Quinoidal Structures for Organic Field Effect Transistors	Geng Yanhou & Chi Chunyan
	15:00-15:20	Jin Tengyu	Native Oxide Dielectric Based Flash Memory and Artificial Synapse	Chen Wei
	15:20-15:40	Zhang Qing	Centimeter-Scale Crystalline Poly(3-hexylthiophene) Film via Space-Confined Drop-Casting towards Photonic Synaptic Transistors	Hu Wenping & Chen Wei
	15:40-16:00: Break			
	Session Chair: An Chuanbin			
	16:00-16:20	Wang Congyong	Conductive Metal-Organic Frameworks Based Tandem Catalysts for Electrocatalytic CO_2 Reduction	Hu Wenping & Wu Jishan
	16:20-16:40	Zhu Xiaoting	Organic radicals for OFET based electronic and magnetic application	Hu Wenping & Wu Jishan
	16:40-17:00	Zhou Qifeng	Synthesis of Belt-shaped π-Conjugated Carbon Nanostructures	Wu Jishan
	17:00-17:20	Xin Shan	The Aromaticity of Expanded Radialenes and Its Charged Species	Wu Jishan
	17:20-17:40	Zhang Qiuyu	Indenofluorene Macrocyclic Oligomers	Wu Jishan

Center 2: Organic Chemistry				
Symposium Chair: Lin Zhikeng				
		Presenter	**Title**	**Supervisor**
Session Chair: Lin Zhikeng				
Morning	9:00-9:20	Wang Junjie	Enantioselective Phosphine-Catalyzed γ-Addition: Divergent Total Synthesis of Aspidosperma Alkaloids	Lu Yixin
	9:20-9:40	Li Rui	One-pot Cyclization & [3,3]-Rearrangement Approach to Access BINAM Derivatives	Lu Yixin
	9:40-10:00	Zhu Kun	Sulfonylarylation of 1,3-Enynes via Dual Nickel and Photoredox Catalysis	Lu Yixin
	10:00-10:20	Lin Zhikeng	Rhodium-catalysed Enantioconvergent Isomerisation of Homoallylic Amines	Zhao Yu
	10:20-10:40	Gao Yaru	Asymmetric Synthesis of N-N Linked Axially Chiral Bipyrroles	Zhao Yu
	10:40-11:00: Break			
	Session Chair: Lin Zhikeng			
	11:00-11:20	Pan Jiaoting	Iridium-catalyzed Enantioselective Isomerization of Alkenyl Indolines	Zhao Yu
	11:20-11:40	Dong Xiaohan	Phosphine-Catalyzed Asymmetric Annulation of Allenoates with Alkenes and Subsequent Visible-Light-Induced Decarboxylation Reactions	Ma Jun'an & Lu Yixin
	11:40-12:00	Yuan Ye	Photo-induced Decarboxylative Multifluoroarylation of Carboxylic Acids	Ma Jun'an & Wu Jie
	12:00-12:20	Zhao Taoqian	Cobalt-catalyzed Regio-divergent and Enantioselective Hydroboration/ Cyclization of Dienynes	Ma Jun'an & Ge Shaozhong
Lunch Break				

Center 2: Functional Materials				
Symposium Chair: Liu Zhihe				
		Presenter	**Title**	**Supervisor**
Session Chair: Liu Zhihe				
Sym2	14:00-14:20	Zhang Shiyu	Novel Nanofiltration Membranes for Mg^{2+}/Li^{+} Separation	Jiang Zhongyi & Zhang Sui
	14:20-14:40	Pu Yunchuan	Hydrolyzed PIM-1 Mixed Matrix Membranes with Amino-Functionalized NUS-8 Nanosheet Fillers for CO_2 Separations	Jiang Zhongyi & Zhao Dan
	14:40-15:00	Xie Silijia	Nanobubble Regulated Hierarchical Enzyme@ZIF-8 Composites with Enhanced Catalytic Activity	Jiang Zhongyi & Zhang Sui
	15:00-15:20	Gong Xiaoting	Design and Synthesis Nanoparticles with AIE Feature for Transparent Mouse Brain Vascular Imaging	Liu Bin
	15:20-15:40	Cheng Wei	Multimodal Imaging Guided Photothermal Therapy for Targeted Brain Tumor Treatment	Liu Bin
	15:40-16:00: Break			
	Session Chair: Zhang Bihan			
	16:00-16:20	Liu Zhihe	Tailoring the Intrinsic Conductivity of Gold Nanoclusters Through Ligand Engineering for Electrocatalysis	Xie Jianping
	16:20-16:40	Lin Yingzheng	Revealing the Structural Evolution of $(Ag/Au)_{44}SR_y$ Clusters through the Inter-Cluster Reaction between $[Ag_{44}(SR)_{30}]^{4-}$ and $[Au_{44}(SR)_{26}]^{2-}$	Xie Jianping
	16:40-17:00	Zhang Bihan	Strong Acid Functionalized Gold Nanoclusters for Enhanced Physicochemical Properties	Xie Jianping
	17:00-17:20	Liu Zhuang	Lanthanide-doped Halide Perovskites for Optoelectric Applications	Liu Xiaogang
	17:20-17:40	Gao Xiong	Non-radiative Energy Dissipation in Photoexcited Organic Charge Transfer Crystals	Hu Wenping & Liu Xiaogang
	17:40-18:00	Zhao He	All Inorganic Perovskite Based Direct X-ray Detectors	Gong Jinlong & Liu Xiaogang

Center 3: Energy Storage and Electrocatalysis				
Symposium Chair: Wang Meng				
		Presenter	**Title**	**Supervisor**
Symposium Chair: Wang Meng				
Morning	9:00-9:20	Lu Haotian	Stable Lithium Metal Anode Enabled by 3D Lithiophilic Current Collector	Yang Quanhong & Chen Wei
	9:20-9:40	Wang Lu	Covalent-Organic-Framework-Modified Zinc Anode for High-Performance Zn-Ion Batteries	Yang Quanhong & Loh Kian Ping
	9:40-10:00	Wang Feifei	Single-Atom Electrocatalysts for Lithium Sulfur Batteries	Yang Quanhong & Lu Jiong
	10:00-10:20	Ma Yuhan	3D Carbon as Inorganic Filler toward Stable Composite Solid-State Electrolyte for All Solid-State Li Metal Battery	He Chunnian & Wesley Zheng Guangyuan
	10:20-10:40	Luo Yani	A Unique Electrolyte Additive for the Improved Electrochemical Performance of Li-O_2 Batteries	Chen Wei
	10:40-11:00: Break			
	Session Chair: Wang Meng			
	11:00-11:20	Da Yumin	Atomically Dispersed Ni-N-C Decorated with Pt toward Hydrogen Evolution Reaction	Hu Wenbin & Chen Wei
	11:20-11:40	Yan Zhicheng	MOF-based Material for Electrocatalytic Application	He Chunnian & Loh Kian Ping
	11:40-12:00	Zhang Hanwen	Gas Phase Salt Assisted Synthesis Advanced 2D Material	He Chunnian & Sow Chorng Haur
	12:00-12:20	Liu Yuan	In-situ Spectroscopy Investigation of Alkali Metal Interaction Mechanism with Organic Semiconductor for Li-Anode	Chen Wei
Lunch Break				

Centre 3: Catalysis				
Symposium Chair: Zheng Ying				
		Presenter	**Title**	**Supervisor**
Session Chair: Zheng Ying				
Sym2	14:00-14:20	Wang Wei	Chemical Looping Oxidative Dehydrogenation of Propane On Redox Catalysts	Gong Jinlong & Chen Wei
	14:20-14:40	Shi Xiangcheng	Genetic Algorithm for Global Structure Optimization of Catalytic Surface System	Gong Jinlong & Wu Jie
	14:40-15:00	Tang Jie	Energy Conversion for CO_2 Hydrogenation and H_2 Production	Gong Jinlong & Sibudjing Kaw & Ho Ghim Wei
	15:00-15:20	Wong Sie Shing	Promoting Photocatalytic Formic Acid Decomposition via Transient Illumination	Yan Ning
	15:20-15:40	Li Haoyue	Using N_2 as a Feedstock for Organonitrogen Chemicals	Yan Ning
	15:40-16:00: Break			
	Session Chair: Zheng Ying			
	16:00-16:20	Wang Sikai	Methane Conversion into Value-Added Organic Chemicals	Yan Ning
	16:20-16:40	Han Xiaoyu	CO_2 Hydrogenation to Methanol Based on Zr-MOF Catalyst	Ma Xinbin & Sibudjing Kawi
	16:40-17:00	Wu Zhongjie	Carbon Capture and Low-Temperature Conversion Using Metal-Organic Frameworks	Ma Xinbin & Zhao Dan
	17:00-17:20	Zheng Ying	The Relationship between Catalytic Performance and the Active Site Structure for Single-atom Catalysts	Ma Xinbin & Yan Ning

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Wood-Based Single Atom Catalysts for Efficient Construction of Substituted Quinolines

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Abstract

The production of high-value chemicals by single atom catalysis is an attractive proposition for industry owing to its remarkable selectivity. Successful demonstrations to date are mostly based on gas-phase reactions, and reports on liquid-phase catalysis are relatively sparse owing to the insufficient activation of reactants by single atom catalysts (SACs) as well as their instability in solution. Here, we have developed mechanically strong, hierarchically porous wood plates for the immobilization of SACs to enhance catalytic activity and stability. Our wood-based SACs exhibit excellent activity and selectivity (~ 68%) towards the synthesis of substituted quinolines by a three-component oxidative cyclization, affording a wide assortment of quinolines (23 examples) from feedstock anilines and acetophenones in an efficient, atom-economical manner. Particularly, a Cavosonstat derivative can be synthesized through a one-step, Fe1-catalysed cyclization instead of traditional Suzuki coupling. Our strategy is also applicable to the deuteration at the 4-position of quinolines, which is challenging by conventional methods. The synthetic utility of our wood-based SAC, together with its reusability and scalability, renders it promising for industrial productions.

Publication List

Chen, Z.; **Song, J.**; Peng, X.; Xi, S.; Liu, J.; Zhou, W.; Li, R.; Ge, R.; Liu, C.; Xu, H.; Zhao, X.; Li, H.; Zhou, X.; Wang, L.; Li, X.; Zhong, L.; Rykov, A.; Wang, J; Koh, M. J.; Loh, K. P. Wood-Based Single Atom Catalysts for Efficient Construction of Substituted Quinolines. Manuscript submitted.

Metallo-Covalent Organic Frameworks

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Abstract

The discovery of graphene has inspired great efforts devoted to the rational synthesis of organic 2D materials because of its unique properties from the long-arranged structures on two surfaces (on both sheet sides), and on the 1D circumference.

Synthesizing ultrathin organic 2D materials is still challenging, but continue efforts have been done in synthesis strategies like (1) Locking intra-layer rotation; (2) Vertical charge repulsion; (3) Growth on surface/interfaces.

Here, a new strategy using vertical hinderance to get ultrathin 2D organic materials was proposed and proved. However, synthesizing materials with high crystallinity is still on trying. And there still is a lack of mechanistic understanding of the process, which needs more in-situ structural proofs.

Publication List

None

Chemical Vapor Deposition of MoO_xSe_y and its Electrical Transport Property

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Abstract

The complete conversion of transition metal oxides (TMOs) into transition metal dichalcogenides (TMDs) have been studied for decades, aiming to form defect-free 2D crystalline products in the chemical vapor deposition (CVD). Even though the oxygen in the TMDs is usually believed to have negative effect on the properties of materials, the intermediate state between TMOs and TMDs may show different properties due to the asymmetry structure raised by the exchange between oxygen and chalcogen atoms. In this work, we studied the formation and properties of MoO_xSe_y. MoO_xSe_y is grown under controlled Se evaporation conditions to obtain different Se concentration in the products. The morphology of MoO_xSe_y is observed by both optical microscopy (OM) and scanning electron micro scopy (SEM). Energy dispersive X-ray spectroscopy (EDS) is used to determine the ratio of Mo/Se in the MoO_xSe_y. X-ray diffraction (XRD) is carried out and the results indicate the coexistence of MoO_2 and $MoSe_2$. The transport property of MoO_xSe_y is measured through the direct deposition of Ti/Au electrode (top electrode) on the MoO_xSe_y film, which is grown directly on the high conductive silicon (bottom electrode). It turns out that when the Se concentration is low, the electric behavior of MoO_xSe_y is similar to the metallic MoO_2. Hysteresis loop appears in $MoO_xSe_{0.83}$ in the voltage range of -4.5~4.5 V. This results indicate MoO_xSe_y to be a potential memristive materials.

Publication List

None

Design and Function of π Electronic Covalent Organic Frameworks

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Abstract

Covalent organic frameworks (COFs) are a class of crystalline porous polymer which can be designed by topology diagram and synthesized via polycondensation reactions to produce organic materials with highly ordered structures. Advances in the chemistry over the past 15 years have shown our capability of designing organic materials with discrete architectures and pores, establishing the basis of the field.[1,2] Indeed, COFs feature a broad diversity of building blocks, wide scope of linkages, and a variety of different topologies, rendering the frameworks and materials able to trigger distinct interplays with photons, electrons, ions, and molecules. Owing to the predesignability, COFs offer an irreplaceable platform for bridging the boundary of chemistry and materials science to enable the bottom-up design of functions.

We are interested in exploring COFs to create designable architectures and unique functions. In this project, we focus on designing the skeletons and pores of COFs to achieve predesigned π electronic structures. In this meeting, we will report the literature review, backgrounds and progress of experimental studies.

Publication List

1. **Li, Z.**; He, T.; Gong, Y.; Jiang, D. Covalent Organic Frameworks: Pore Design and Interface Engineering. *Acc. Chem. Res.* **2020**, 53, 1672–1685.
2. Liu, R.; Tan, K. T.; Gong, Y.; Chen, Y.; **Li, Z.**; Xie, S.; He, T.; Lu, Z.; Yang, H.; Jiang, D. Covalent organic frameworks: an ideal platform for designing ordered materials and advanced applications. *Chem. Soc. Rev.* **2021**. DOI: 10.1039/d0cs00620c.

Design and Synthesis of Novel Architectures of Covalent Organic Frameworks

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Abstract

Covalent organic frameworks (COFs) represent an emerging class of crystalline porous polymer which can be constructed with organic building blocks by topology-directed polymerization. Especially, COFs exhibit unique porous features and skeleton characteristics which are distinct from other polymers and porous materials. Progress over the past 15 years in the design and synthesis has greatly expanded the structural diversity and functional scope and deepened our understandings of interplays of COFs with ions and molecules.

We are interested in exploring COFs to design discrete structures and to develop unique functions through topology-directed polymerization of different organic building units. In this project, we are interested in exploring COFs to construct different topologies and lattices by merging covalent bonds with noncovalent interactions into one-pot polymerization systems. This strategy will enable us to develop the ordered yet extended structures into all dimensions in a controlled manner. In this meeting, we will report the literatures, research backgrounds, and progress in experiments.

Publication List

Liu, R.; Tan, K. T.; Gong, Y.; Chen, Y.; Li, Z.; **Xie, S.**; He, T.; Lu, Z.; Yang, H.; Jiang, D., Covalent organic frameworks: an ideal platform for designing ordered materials and advanced applications. *Chem. Soc. Rev.* **2021.** DOI: 10.1039/D0CS00620C

Designed Synthesis of Novel Covalent Organic Frameworks

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Abstract

Covalent organic frameworks (COFs) are a class of crystalline porous polymer that enables integration of organic building units into periodic networks and order pores. Progress over the past decade in chemistry has greatly enhanced our capability of designing COFs to achieve atomically precise organic architectures. Especially, the diversity of building blocks, the variety of linkages, and the scope of topologies provide chemical basis of structural diversity and multifunctionality of COFs. These achievements showed the great potential of the field and established a molecular platform for creating organic/polymeric materials to develop a diversity of different functions which are specific to their structures.[1]

We are interested in exploring COFs to construct highly ordered organic structures and to develop unique functions by elucidating the interplays of frameworks with different elementary particles including photons, electrons, holes, spins, and charges. In this project, we focus on designing a novel class of COFs. In this meeting, we will report the literature survey, backgrounds, and experimental progress.

Publication List

Liu, R.; Tan, K. T.; Gong, Y.; Chen, Y.; Li, Z.; Xie, S.; He, T.; Lu, Z.; **Yang, H.**; Jiang, D., Covalent organic frameworks: an ideal platform for designing ordered materials and advanced applications. *Chem. Soc. Rev.* **2021**. DOI: 10.1039/D0CS00620C

Development of Novel NIR Organic Dyes with AIE Properties for Sensitizing NIR-II luminescence of lanthanides Doped Nanocrystals

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Abstract

Sensitizing lanthanide doped nanocrystal with organic dyes have been widely employed in numerous fields, ranging from biological imaging, volumetric displays, to solar cells. Significantly, the narrow spectral window and small absorption cross-section of lanthanide ions can be ameliorated tremendously by introducing organic molecule as antenna. However, the sensitization efficiency is still limited due to the aggregation-caused quenching (ACQ) and poor photostability of conventional dyes. Herein, we are committing to develop novel NIR dye with excellent aggregation-induced emission property (NIR-AIEgens), named triphenylamine-benzobisthiadiazole derivative (TPA-BBT). Donor-acceptor structure is designed, by combining electron-donating group triphenylamine and strong electron-accepting group benzobisthiadiazole, to achieve the bathochromic shift emission of the TPA-BBT, which can match well with the absorption of sensitizers Nd^{3+} within nanocrystal. Meanwhile, the triphenylamine with highly twisted molecular backbone would assist in preventing close packing and reducing intermolecular interactions. Subsequently, abundant TPA-BBT is anchored to the surface of $NaYF_4$:Nd,Er@$NaYF_4$:Nd nanocrystal by virtue of the coordination between carboxyl and lanthanide ions. Effective NIR-II emission originating from activator Er^{3+} can be achieved after excitation of TPA-BBT. With this NIR-AIEgens sensitized nanocrystal, the drawbacks about the unfavorable ACQ and the poor photostability can be overcome perfectly. Moreover, loading amount of NIR-AIEgens per unit area on the surface of nanoparticles can be elevated comparing with conventional dyes, which permits more sensitizers Nd^{3+} to involve in the energy transfer process and allows for an increase in sensitization efficiency. This work hopes to provide a new avenue for NIR-AIEgens-sensitized nanocrystal to surmount a series of fundamental bottlenecks.

Publication List

None

The Derivatives of Triphenylamine with Room Temperature Phosphorescence

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Abstract

Organic room temperature phosphorescent materials are known for their synthetic feasibility, tunable phosphorescence wavelength and lifetime, etc. Hence new design strategies have been applied on various fluorophores to improve phosphorescence features. Among those, triphenylamine derivatives are phosphorescence active due to the presence of nitrogen atom and intermolecular interactions in the crystal state. Here we have studied the room temperature phosphorescence of two triphenylamine derivatives with various functional groups (4,4',4''-tri[boronic acid] triphenylamine and 4,4',4''-tricarboxyl triphenylamine). Detailed studies would be carried out to investigate the relationship between the phosphorescence and respective functional group modification. A long phosphorescence lifetime at room temperature in air is expected to be achieved by the interplay of strong intermolecular interactions, efficient intersystem crossing using functional group variation. In addition, mechanoluminescence (ML) is also expected to be achieved in triphenylamine derivatives. Thisemission maybe packing-dependent, so it is necessary to analysetheir optical properties, intermolecular interactionsand crystal structures in these triphenylamine derivatives, which can guide the reasonable design of organic molecules with special light-emission properties.

Publication List

None

Tailoring Crystal Facets of Different Catalysts to Enhance Photocatalytic Activity for Hydrogen Evolution

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Abstract

The introduction of cocatalyst has been well established to be the most effective way to suppress the charge recombination, provide adequate active sites and reduce activation energy for hydrogen evolution. Noble metals (e.g: Pt, Pd) are well known as the most used and efficient cocatalysts. However, their high-cost and limited-reserves drive the demand to explore non-precious metal cocatalysts with low cost and high efficiency. Metal-organic frameworks (MOF) are porous crystalline materials built by the combination of metal ions and clusters with organic linkers. MOFs are emerging in the field of photocatalysis due to their tailorable capacity to absorb light by the judicious selection of metal cluster and organic linkers. Nickel (Ni) based materials are increasingly used in many fields possessing excellent catalytic active for hydrogen evolution. We explore here the synthesis of the Ni-based metal-organic layer (MOL), Ni-MOL, exposing rich (100) crystal facets (Ni-MOL-100) (687.8 μmol g^{-1}) shows a much higher photocatalytic hydrogen evolution activity than the one exposing rich (010) crystal facets (Ni-MOL-010) (56.8 μmol g^{-1}) and its bulky counterpart (bulky Ni-MOF) (0.0 μmol g^{-1}), respectively.

Publication List

None

Synthesis and Characterization of Multiblock Stretchable Polymer Semiconductors Based on PBTTT

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Abstract

With the development of science and technology, wearable electronic devices have entered people's sight. As the essential elements of stretchable electronic devices for wearable electronics, OTFTs need to be stretchable and mechanically robust in addition to high mobility. Intrinsically stretchable polymer semiconductors are essential because organic conjugated polymers are particularly suitable for the preparation of large-area and flexible devices. Previous studies on stretchable semiconductors mostly focused on the tensile properties of the materials and ignored the elastic recovery properties of the materials. However, elastic recovery properties should be very important in wearable electronic devices.

Thermoplastic elastomers (TPEs) combine the mechanical strength and elastic properties of thermoplastic and vulcanized rubber. If the mechanical properties of organic conjugated polymers can be improved to the similar content to that of TPEs, such polymers will be one step closer to practical applications. Rod-coil-rod triblock and multiblock copolymers are effective methods for preparing TPEs and adjusting phase structure due to self-assembly capability of block copolymer. Herein, multiblock stretchable polymer semiconductors were synthesized. The hard segment (rod segment) selected was Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT), and the soft segment (coil segment) selected was hydrogenated hydroxy terminated polybutadiene (H-HTPB) with appropriate molecular weight of M_n = 1500. The preliminary results showed that these block copolymers have good mechanical properties. More detailed mechanical and electrical properties need to be further characterized.

Publication List

None

π-Conjugated Molecules with Quinoidal Structures: Synthesis, Properties and Applications

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Abstract

In recent years, quinoids as a novel class were widely studied in many fields because of the unique electrical, optical, and magnetic properties. Pyromellitic diimide and phthalimide-based quinoid is constructed by terminated with a new terminus 1,3-indandione. Pyromellitic diimide and phthalimide-based quinoids terminated with 1,3-indandione is hopefully applied into OFETs. Up to now, the precursor has been successfully obtained. Compared with one dimensional linear quinoids, two dimensional π-extended quinoids exhibit enhanced semiconducting properties. Thieno[3,4-b]thiophene (TbT) displays intrinsic low aromaticity in constructing π-extended quinoids. Quinoidal TbTs terminated with 1,3-indandione are designed and the synthesis of them is currently underway.

Publication List

None

π-Conjugated Materials with Quinoidal Structures for Organic Field Effect Transistors

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Abstract

Organic field effect transistors (OFETs) have been gained much attention because of the potential applications on radio frequency identification devices (RFID), electronic skin and kinds of sensors. With great interest on the research of organic semiconductors (OSCs), large number of studies on the materials design have been undergoing. Herein, π-conjugated materials with quinoidal structure have been widely believed as a good potential semiconductor material for OFETs. Herein, π-conjugated quinoids with isoindigo-based and its derivatives thienoisoindigo-based as the building block substituted with cyanoquinomethane termini and large fused ring π-conjugation are designed and will be synthesized and prepared for OFETs to explore the relative physicochemical properties and device performance.

Publication List

None

Native Oxide Dielectric Based Flash Memory and Artificial Synapse

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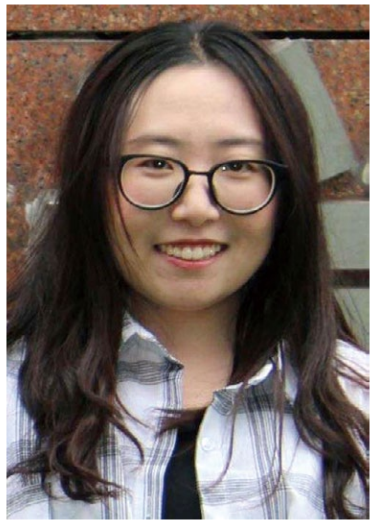
Abstract

Two-dimensional (2D) materials based artificial synapses are important building blocks for the brain-inspired computing systems that are promising in handling large amounts of informational data with high energy-efficiency in the future. However, 2D devices usually rely on deposited or transferred insulators as the dielectric layer, resulting in various challenges in device compatibility and fabrication complexity. Here, we demonstrate a controllable and reliable oxidation process to turn 2D semiconductor HfS_2 into native oxide, HfO_x, which shows good insulating property and clean interface with HfS_2. We then incorporate the HfO_x/HfS_2 heterostructure into a flash memory device, achieving a high on–off current ratio of ~10^5, a large memory window over 60 V, good endurance and long retention time over 10^3 seconds. Especially, the memory device can work as an artificial synapse to emulate basic synaptic functions and feature good linearity and symmetry in conductance change during long-term potentiation/depression processes. A simulated artificial neural network for MNIST pattern recognition can be realized based on our synaptic device. Our work provides a simple and effective approach for integrating high-k dielectrics into 2D material-based memory and synaptic devices.

Publication List

1. **Jin, T.**; Zheng, Y.; Gao, J.; Wang, Y.; Li, E.; Chen, H.; Pan, X.; Lin, M.; Chen, W. submitted
2. Pan, X.; **Jin, T**.; Gao, J.; Han, C.; Shi, Y.; Chen, W. *Small* **2020**,16, e2001504.

Centimeter-Scale Crystalline Poly(3-hexylthiophene) Film via Space-Confined Drop-Casting towards Photonic Synaptic Transistors



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Abstract

Brain-inspired neuromorphic computing aims to address the issues in Von-Neumann-based computation. In the biological neural network, signals can be transmitted by the modulation of synaptic weight. This has inspired significant research efforts to imitating synaptic functions through electronic devices. Conjugated polymers have been widely employed in synaptic transistors owing to none biological rejection and flexibility. However, controllable preparation of high-quality conjugated polymers with high efficiency is still challenging. Ultrafast space-confined drop-casting is newly developed to realize controllable fabrication of a centimeter-scale poly(3-hexylthiophene) (P3HT) membrane with high crystalline in a very few minutes. The thickness of the as-produced P3HT films can be as thin as two molecular layers. With a combination of an additional dielectric gate offering electron trapping states, photonic synaptic transistors (PSTs) have been successfully constructed. Under the modulation of light, this device performs typical synaptic functions, including short-term plasticity, long-term plasticity, paired-pulse facilitation, spike-intensity-dependent plasticity and spike-time-dependent plasticity. Moreover, the PSTs can operate stably even after two months, demonstrating a high device durability. Our work largely improves the preparation efficiency of synaptic transistors and lays a foundation on large-area integrated wireless communication system and artificial visual system.

Publication List

1. **Zhang, Q.**; Ye, X.; Zheng, Y.; Wang, Y.; Gao, Z.; Wu, J.; Dong, H.; Geng, D.; Chen, W.; Hu, W. Centimeter-Scale Crystalline Poly(3-hexylthiophene) Film via Space-Confined Drop-Casting towards Photonic Synaptic Transistors. (In preparation)
2. **Zhang, Q.**; Jin, T.; Ye, X.; Geng, D.; Chen W.; Hu, W. Organic-Field-Effect-Transistors-based Photonic Synapses: Progress and Perspectives. (In preparation)

Conductive Metal-Organic Frameworks based Tandem Catalysts for Electrocatalytic CO_2 Reduction

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Abstract

The large-scale depletion of fossil fuels has substantially increased the CO_2 concentration in atmosphere, resulting in a series of environmental issues such as glacial melting and global warming. The electrochemical reduction of CO_2 to value-added fuels and chemicals represents an attractive pathway for migrating CO_2 emission issue and achieving the storage of renewable energy. Recently, metal-organic frameworks (MOFs), as a novel class of reticular materials built from inorganic metal/cluster nodes and organic ligands, have emerged as suitable electrocatalysts for CO_2 reduction reaction (CO_2RR) due to their unique advantages of tunable structure, accessible incorporation of actives sites, outstanding surface areas, remarkable stability, and highly exposed catalytic sites. However, the majority of MOFs suffer from inherently low conductivity, hindering their electrocatalytic performances toward CO_2RR. Moreover, it remains a great challenge to prepare high-performance MOFs-based electrocatalysts that can produce more valuable multi-carbon products (C_2H_4, C_2H_5OH, eg.) with high selectivity and activity. To address these issues, a strategy of constructing conductive MOFs-based tandem catalysts is proposed. Since copper is an efficient metal in reducing CO_2 into multi-carbon products, we aim to construct tandem catalysts based on Cu-based conductive MOFs and noble metals (Au, Ag, and Pd). It is anticipated that conductive Cu-MOFs based tandem catalysts can effectively produce multi-carbon products through CO_2 reduction to CO on noble metals andsubsequent carbon-carbon coupling on Cu nodes of MOFs.

Publication List

1. **Wang, C. Y.**#; Yang, C. H.#; Zhang, Z. C. Unraveling molecular-level mechanisms of reactive facet of carbon nitride single crystals photocatalyzing overall water splitting. *Rare Metals.* **2020**, 39, 1353-1355.
2. Gao, Z. Q.#; **Wang, C. Y.**#; Li, J. J.; Zhu, Y. T.; Zhang, Z. C.; Hu, W. P. Conductive Metal-Organic Frameworks for Electrocatalysis：Achievements, Challenges, and Opportunities. *Acta Phys. -Chim. Sin.* **2020**, 37, 2010025.

Organic Radicals for OFET Based Electronic and Magnetic Application

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Abstract

Organic radicals are paramagnetic molecules that have unpaired electrons (S =1/2). On one hand, metal-like electrical properties can be formed by the half-filled orbital, on the other hand, semiconducting properties can be generated due to Coulomb interactions between the unpaired electrons. Therefore, organic radicals are expected to hold unique electrical and magnetic properties. Recent study shows OFETs based on radicals have excellent charge transport ability due to the dense packing by the spin-spin interaction. However, the instability of organic radicals hinders their practical applications. Here we designed a pair of radical Isomers (2,3:10,11-Dibenzoheptazethrene and 4,5:12,13-Dibenzoheptazethrene) with good air stability. OFETs based on single-crystalline DBHZ3 and DBHZ4 showed highest hole mobility of 0.17 cm^2 V^{-1} s^{-1} and 0.05 cm^2 V^{-1} s^{-1}. The OFET devices also showed excellent air stability after 18 times sweep and mobility only have slightly drop after 2 months in air, which indicates the potential application prospect in organic electronic devices.

Publication List

Zhang, Y., Yang, S., **Zhu, X.**, Zhai, F., Feng Y., Feng W., Zhang X., Li R., Hu, W. *Sci. China, Chem.* **2020**, 63, 973-979. (co-first author)

Synthesis of Belt-shaped π-Conjugated Carbon Nanostructures

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Abstract

The selective synthesis of well-defined π-conjugated carbon nanostructures has been attracting increasing interest because these nanostructures can server as carbon nanotube (CNT) segments for achieving the long-standing goal of synthesizing structurally uniform CNTs. Among these nanostructures, belt-shaped π-conjugated carbon nanostructures are quite challenging targets in both carbon science and organic synthesis chemistry and are key steps toward achieving the holy grail of single-walled CNTs. In this project, we try to construct a series of carbon nanobelts to enrich the system of CNT segments. In order to overcome the intrinsic strain and high reactivity, we employ oxygen-bridged building block as strain buffering moiety and incorporate bulky groups in reactive sites to stabilize the expected compounds. Based on our previously systematic studies in the construction of π-conjugated carbon nanostructures and our comprehensive considerations of the rational design, a feasible synthetic route is developed. The chirality and topology of carbon nanostructures are also of great interest to us; thus, we are planning to construct some helical carbon nanobelts and even Möbius belts. Helicene derivative is chosen as the chiral unit, which eases to form twisted macrocycle in the cyclization step. Except for intricate connectivity and topology, these chiral nanobelts may also exhibit unique and unexpected properties, such as fascinating optical properties, special magnetic properties and even global aromaticity following Möbius rule and so forth.

Publication List

None

The Aromaticity of Expanded Radialenes and Its Charged Species

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Abstract

Radialenes, a series of all-methylidene-substituted cycloalkanes of molecular formula CnHn, arecross-conjugated all sp2-hybridized rings and carry as many exocyclic double bonds as possible. Inserting of ethane-1,2-diyl or buta-1,3-diyne-1,4-diyl fragments between each pair of vicinal exo-methylene units in the framework of radialenes form the expanded radialenes with large conjugated all-carbon cores, which have attracted substantial theoretical and experimental study. However, theoretical studies have shown the macrocyclic cores of these molecules usually present poor aromatic character, while the dianionic ones exhibit enhanced aromaticity. Despite the remarkable properties predicted by theoretical calculations, experimentally exploring the aromaticity of these compounds and their charged species are still attractive. Herein, we synthesize a series of 9-fluornylidene substituents extended radialenes and systematacially investigate the aromatic characters of these molecules. The X-ray crystallographic analysis revealed the planar backbone of the neutral compound. The electrochemical properties were investigated by cyclic voltammetry and differential pulse voltammetry. The chemical reduction was successfully carried out by treating with single electron transfer reductant sodium anthracene. The magnetic properties of the reduced species were studied by NMR, which indicated the enhancement of the aromaticity of the macrocyclic core and suggested a charge separated form. Meantime, we intend to confirm the structure of the anionic compound by growing single crystal. Furthermore, we carried out theoretical calculations to studied the structural, electronic, optical and magnetic properties of these compounds.

Publication List

None

Indenofluorene Macrocyclic Oligomers

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Abstract

Indenofluorenes are unique biradicaloid compounds with five fused 6-5-6-5-6 membered rings. The biradical character of five indenofluorene isomers have been widely studied. Also, indenofluorenes show unique optical properties due to the five membered rings.

Among the five structural isomers of indenofluorenes, it is demonstrated that Indeno[2,1-b]fluorene has a larger singlet biradical character than its other isomers. Therefore, in our project, the macrocycle based on Indeno[2,1-b]fluorene was designed. The designed compound was synthesized by Yamamoto coupling followed by reduction with tin(II) chloride. It is assumed that the two structural isomers of the designed macrocyclic compound may exist at the same time. The valence tautomerization between two resonance structure can then be studied by VT NMR. X-ray crystallographic analysis will be conducted to confirm the structure of the macrocycle compounds. The optical and electrochemical properties of the compounds will be investigated by UV-Vis-NIR spectroscopy and cyclic voltammetry. Theoretical calculations will also be performed to illustrate the aromatic characteristics of the compounds.

Publication List

None

Enantioselective Phosphine-Catalyzed γ-Addition: Divergent Total Synthesis of *Aspidosperma* Alkaloids

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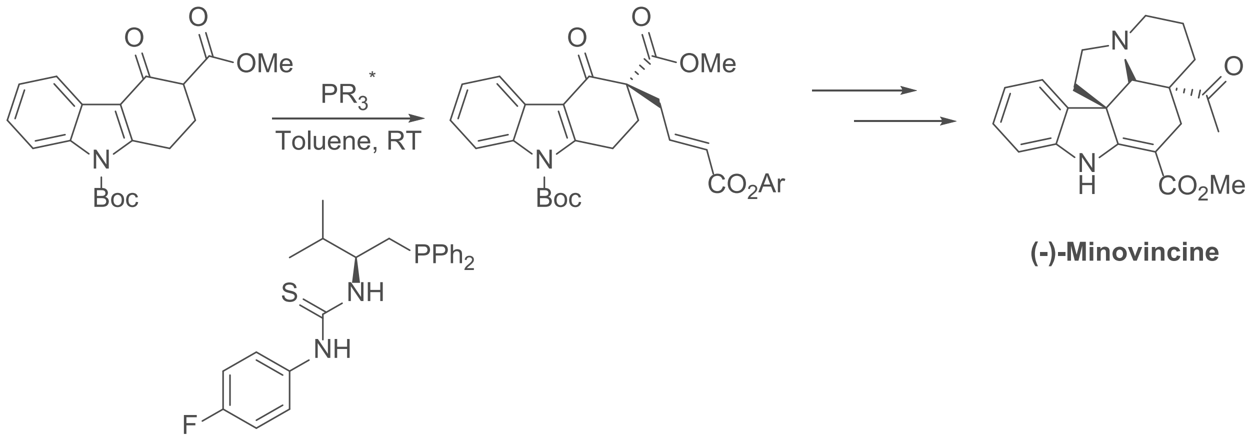
Abstract

Phosphine-catalyzed the asymmetric γ-additions of carbazolones to allenoates to afford 3,3-disubstitutedcarbazoloneshave been established. Different substituted carbazolones could be employed in this process, whichis catalyzed bya chiral phosphine derived from an amino acid, affording 3,3-disubstituted carbazolonesin good yield and excellent enantioselectivity. This methodology will be applied in total synthesis of *Aspidosperma* alkaloid. Thekey synthetic features include a reductive-amination cyclization and nucleophilicsubstitution cyclization to installits key carbocyclic skeleton. This strategy will be applicable for assembling divergent *Aspidosperma* alkaloids possessing this key skeleton.



Publication List

None

One-pot Cyclization & [3,3] Rearrangement Approach to Access BINAM Derivatives

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Abstract

Axial chiral biaryl compounds have important applications in organic chemistry. They often act as ligands in many catalytic enantioselective transformations. Axial chirality is also a key feature of many natural products and most of them exhibit outstanding biological activities including vancomycin, streptonigrin and michellamines. As a result, there are few methods available for their atroposelective synthesis including dynamic kinetic resolution, desymmetrization, transition-metal catalyzed direct biaryl coupling, atroposelective biaryls synthesis and traceless central-to-axial chirality exchange.

Although the synthetic methods are influential, more efficient and powerful strategies are needed to complement current methods. [3,3]-Rearrangement is a powerful method to construct a new C(sp^2)-C(sp^2) bond between two aromatic rings at the expense of an N-N bond. The method has been successfully applied in the synthesis of axial chiral compounds. However, there are only two cases published which suffer from limited scope, poor enantioselectivity and unstable starting material.

Based on the background, our group recently focus on developing a novel and powerful strategy to access axially chiral biaryls through one-pot cyclization and [3,3]-rearrangement process. Asymmetric cyclization has achieved great progress and most of them delivered products in excellent enantioselectivity. Therefore, we envision that combining cyclization with [3,3]-rearrangement could be an efficient approach to control enantioselectivity and access large scope of BINAM derivatives.

Publication List

None

Sulfonylarylation of 1,3-Enynes via Dual Nickel and Photoredox Catalysis

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Abstract

Catalytic 1,3-enyne difunctionalization represents an efficient platform for rapid assembly of multifunctional allenes and 1,3-dienes. The long-standing problem observed in addition reactions is the selectivity due to the conjugated structures of 1,3-enynes. Herein, we have developed an unprecedented and straightforward method for the regiodivergent sulfonylarylation of 1,3-enynes via dual nickel and photoredox catalysis. Depending on the nature of the 1,3-enynes, either 1,4-sulfonylarylation takes place, providing efficient access to diverse allenyl sulfones, or 3,4-sulfonylarylation that leads to (E)-1,3-dienyl sulfones with high chemo-, regio- and stereoselectivity. Both of the transformations proceed smoothly under a mild and redox-neutral condition, and display broad substrate scopes and remarkable functional group compatibility. Moreover, the utility of this protocol is demonstrated by the success of gram-scale reactions and further transformation of the generated products.

Publication List

None

Rhodium-catalysed Enantioconvergent Isomerisation of Homoallylic Amines

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Abstract

Chiral amines with remote stereogenic centres are of great importance and present in a wide range of different natural products and drug precursors. Construction of such compounds have been challenging since enantiocontrol by a remote directing/functional group is difficult to achieve. Compared to more well-developed synthesis of remote chiral ketones or alcohols, only a few examples on remote chiral amines have been reported with amination/hydroamination with a consequent cascade chain-walking step. Previously, our group has reported a series of rhodium-catalysed enantioconvergent isomerisation of allylic, homoallylic or bishomoallylic alcohols to access ketones with a remote stereogenic centre in a highly enantioselective manner. Therefore, we think this methodology is transferrable onto similar transformation of alkenyl amines into remotely chiral imines, which may undergo asymmetric hydrogenation or nucleophilic addition to obtain amines with two stereogenic centres with high enantioselectivity and diastereoselectivity. Up to now, good to excellent reactivity has been achieved, yet enantioselectivity is to be improved. Further studies will also include substrate scope, cascade reactions and mechanistic studies.

Publication List

None

Asymmetric Synthesis of N-N Linked Axially Chiral Bipyrroles

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Abstract

Axially chiral biaryl frameworks widely exist in ligands, natural products and drug molecules. Due to its important applications, developing efficient methods to asymmetric synthesis novel types of biaryl atropisomers received many considerations. Compared with the well-developed asymmetric C-C bond linked biaryl atropisomer synthesis and underdeveloped asymmetric C-N biaryl atropisomers synthesis, the N-N bond linked biaryl atropisomers which existed in bioactivity molecules and could be used as potential ligands have not been asymmetric synthesis before.

Based on our group's research on asymmetric condensation reaction, in this work, we successfully designed and asymmetric synthesized both configurations of N-N linked bipyrroles with high conversion and excellent enantioselectivity from 1,4-diketones and aminopyrroles. This method has wide applicability and can simultaneously obtain C2 symmetric and non-C2 symmetric N-N linked bipyrrole products. At the same time, this new type of axially chiral compounds has high configurational stabilities and can be prepared and synthesized in large scale. Meanwhile, the chiral N-N linked bipyrroles can be transferred and used as the potential catalysts and ligands in the field of asymmetric synthesis. In addition, direct asymmetric synthesis of chiral N-N-linked bipyrroles from 1,4-diketone and commercially available hydrazine hydrate is more challenging. A series of work is currently underway, and it is expected to realize this challenge.

Publication List

None

Iridium-catalyzed Enantioselective Isomerization of Alkenyl Indolines

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Abstract

We report herein enantioselective isomerization of alkenyl indolines with a cooperative catalysis of a commercially available iridium catalyst and a chiral phosphoric acid. This methodology gives an alternative way to synthesize chiral alkylated indoles from various achiral alkenyl indolines with high atom economy, simple procedure and easy operation. The alkylated indole products can be obtained in good to high yields. The mechanism of this intramolecular hydrogen transfer undergoes a chain-walking process. Different from other enantioselective intramolecular hydrogen transfer process with alcohols as initial hydrogen resource, this method reported indolines as hydrogen resource.

Publication List

Jiang, Y.; **Pan, J.**; Yang, T.; Lim, J. J. H.; Zhao, Y.; Koh, M. J. *Chem*, in press.

Phosphine-Catalyzed Asymmetric Annulation of Allenoates with Alkenes and Subsequent Visible-Light-Induced Decarboxylation Reactions

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Abstract

Phosphine-catalyzed asymmetric annulation reactions have shown remarkable progress and plays an important role in material synthesis and medicinal chemistry. Among them, [3+2] cycloaddition of alkenes with allenoates is one of the most classical reaction modes and has many valuable works reported, meanwhile, [4+2] cycloaddition gains remarkable progress these years as well. Although these two cycloaddition modes are under great development recent years, only electron-deficient alkenes and allenes could participate in the traditional [3+2] and [4+2] cycloadditions, which leads to over-functionalization of the annulation products bearing at least two electron-withdrawing groups. Recently, N-hydroxyphthalimide (NHP) ester has been demonstrated as an efficient redox-active ester to induce diverse radicals and facilitate photoredox cross-coupling reactions. Herein, I mainly introduce [3+2] and [4+2] annulation reactions between allenes and NHP esters catalyzed by chiral phosphine catalysts. Highly enantioselective five-member ring products are synthesized through this novel [3+2] protocol and broad applications could be realized with further functionalization of the cycloaddition products.

Publication List

None

Photo-Induced Decarboxylative Multifluoroarylation of Carboxylic Acids

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Abstract

C–F functionalizations that provide C–C bonds are challenging synthetic transformations, due in part to the large C–F bond strength, short bond length, nonpolarizable nature, the production of fluoride, and the regioselectivity-in the case of multifluorinated substrates. However, commercially available highly fluorinated arenes possess great synthetic potential because they already possess the C–F bonds in the desired locations that would be difficult to selectively fluorinate. In order to take advantage of this potential, selective C–F functionalizations must be developed. Herein, we design conditions for the photocatalytic reductive alkylation of highly fluorinated arenes with an oxidative decarboxylative from different types of carboxylic acids. So far, the mild reaction conditions provide for a broad functional group scope, such as α-amino, α-oxy and the benzyl carboxylic acids are good substrates to provide relative multifluoroarylation products in a good yield. Further study will concentrate on the scope of different types of multifluorinated arenes and unactivated alkyl carboxylic acid. The mechanism of the reaction is still in the study, the detail will be subjects in future work.

Publication List

None

Cobalt-catalyzed Regio-divergent and Enantioselective Hydroboration/Cyclization of Dienynes

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Abstract

Chiral five-membered carbocyclic and heterocyclic structural motifs are present in diverse bioactive molecules and natural products. Transition-meta-catalyzed cyclization of 1,n-enynes is considered as one of the most straightforward approaches to access cyclic compounds. However, much of the recent work on catalytic boryl-functionalized cyclization of enynes has focused on simple alkenes with few examples of reactions on 1,3-dienes. Here we report the first cobalt (II) catalyzed asymmetric hydroboration/cyclization of dienynes to prepare structurally diverse vinyl boron esters with both 1,4- or 3,4- isomers in good regioselectivities and excellent enantioselectivities. A variety of oxygen-, nitrogen-tethered 1,3,8-dienynes underwent this asymmetric transformation, yielding vinyl-substituted boron esters containing chiral tetrahydrofuran and pyrrolidine moieties with high to excellent enantioselectivities (86%–99% ee). In addition, this transformation can tolerate a variety of mono- or di-substituted dienes and internal dienes, supplemented the structural diversity of previous work on 1,6-enynes. Further studies to reveal the detailed mechanism of this transformation and to develop Co-catalyzed asymmetric hydro-functionalization/cyclization of other multiply-unsaturated substrates will be the subjects of future work.

Publication List

None

Novel Nanofiltration Membranes for Mg^{2+}/Li^{+} Separation

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Abstract

Lithium has aroused more attention due to the rapid development of lithium-ion batteries. Obtaining lithium resource from salt lakes has a great potential, if Mg^{2+}/Li^{+} can be efficiently separated. However, high Mg^{2+}/Li^{+} ratio and relatively low Li^{+} concentration make this separation process need high precision and requirement. As an emerging technology, nanofiltration is promising forthe recovery of Li^{+} from brine due to the minimum energy consumption and facile operation. Because of the similar chemical properties and ion hydration radius of $Mg^{2+}$and Li^{+}, size exclusion is not dominant in separation process. Here we'd like to prepare novel nanofiltration membranes with high positive charges density, expecting the electrostatic repulsion effect will play an important role in obtaining high separation performance in term of permeability and selectivity. In detail, various covalent-organic framework and graphene oxide membranes will be prepared. Compared to traditional polymer-based membranes, these ordered transport pathways enable controlled and precise construction. In conclusion, we expect to improve the current performance of nanofiltration membranes and illustrate transport mechanisms using ordered transport channels.

Publication List

None

Hydrolyzed PIM-1 Mixed Matrix Membranes with Amino-Functionalized NUS-8 Nanosheet Fillers for CO_2 Separations

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Abstract

Carbon dioxide separation based on membrane technology has received intensive interests due to the advantages of low energy consumption, environment-friendly process, smaller equipment investment, etc. However, the trade-off between permeability and selectivity of conventional polymeric membranes largely limits the further development. Considering the intrinsic micropores inside the metal-organic frameworks (MOFs), incorporating the porous MOF fillers into polymer matrix may help to overcome such a trade-off. Nevertheless, the possible filler-matrix interfacial defects can severely reduce the separation performance of the resultant mixed-matrix membranes (MMMs). In this work, highly porous PIM-1 polymer with post-modified carboxyl groups is chosen as the polymeric matrix, and amino-functionalized NUS-8 nanosheet is firstly synthesized as the filler. Benefiting from the increasing hydrogen bonding within the functional groups, the interfacial compatibility between the fillers and the polymer matrix is significantly improved. The as-prepared MMMs with enhanced attractive interaction can accommodate a much high filler loading of 15% with high CO_{2}-selective separation performance.

Publication List

None

Nanobubble Regulated Hierarchical Enzyme@ZIF-8 Composites with Enhanced Catalytic Activity

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Abstract

Enzyme catalysis, referring to green catalytic process of material synthesis and transformation using enzymes as catalysts, sparks much interest in green chemistry. Nevertheless, the fragile nature and nanoscale size of enzymes discount the stability and recyclability, hindering the commercial application of enzyme catalysts. Enzyme immobilization has been widely employed to recycle enzymes and facilitate survival under various challenges. Metal-organic frameworks (MOFs) with high porosity, small apertures, tailorable structure and functions are promising materials. Among them, ZIF-8 has attracted numerous attention due to the ease of synthesis process, biocompatibility of 2-Methylimidazole (HmIM) and mild synthesis condition. However, the extremely small aperture size (0.34nm) of ZIF-8 would increase mass transfer resistance dramatically, which decreases the catalytic efficiency. To address this problem, nanobubbles were introduced in immobilization process to regulate the structure of enzyme@MOF composites, leading to mesopores which can enhance mass transfer. Factors including nanobubble density, component adding order and interval time that influence the final structure and activity have been studied. The results suggest that nanobubbles played a role only when enzymes were added after mixing Zinc solution and HmIM solution. Mesopores introduced by nanobubbles in HmIM or Zinc solutions increased the enzyme composite activity to 2.46 and 2.64 times correspondingly. The activity was further promoted to 3.39 times with nanobubbles appeared in both HmIM and Zinc solutions. Increasing nanobubble density and interval time, the activity was increased accordingly. This study provides a novel one-pot technique to fabricate enzyme catalysis with enhanced activity, which may pave the way for commercial enzyme catalysis.

Publication List

None

Design and Synthesis Nanoparticles with AIE Feature for Transparent Mouse Brain Vascular Imaging

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Abstract

Visualization of cerebral fine vessels is very important for understanding the treatment of vascular dependent diseases such as stroke. However, the research on visualization and whole brain quantification of vascular system by cell resolution is limited. Optical clearing is a procedure that removing the scattering source-refractive index differences within the tissues to obtain the transparent tissues for the visualization of deep structures with a high resolution. However, tissue-clearing technology terms as hydrogen-based method remains unsatisfactory because of the photobleaching of fluorescent dyes or proteins. Herein, combined with the excellent luminescent properties of AIEgens and excellent light penetration depth and high-resolution imaging of tissues-clearing, we design three molecules with AIE features named TTNs, TSNs and TSCNs for 3D reconstruction of vascular network though optical clearing method in mouse brain. This method includes fluorescence labeling by AIEgens, tissue clearing and 3D reconstruction analysis. The highlight of this method is that covalent bonding of fluorophore AIEgens to polyacrylamide to form compact cross-linking hydrogels, ensuring the stable and long-term fluorescence after continuous clearing procedures.

Publication List

None

Multimodal Imaging Guided Photothermal Therapy for Targeted Brain Tumor Treatment

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Abstract

Glioblastoma multiforme (GBM) has been one of the most notorious primary brain malignancies with a strikingly poor survival rate. In clinics, magnetic resonance imaging (MRI) is a commonly utilized imaging tool for diagnosis and post-treatment monitoring of glioma patients with high soft tissue contrast. However, MRI suffers from restrictions such as costly instrumentation and maintenance, and time-consuming data acquisition processes. In recent years, fluorescence-guided (FL) surgery has emerged as an advantageous and complementary technique for surgeons to intraoperatively identify tumor margins and evaluate the extent of tumor tissue resection. On the other hand, photoacoustic imaging (PAI) that hybridizes optical and acoustic imaging modalities exhibits merits of fast real-time scan and relatively deep tissue penetration. Hence, the design of nanocomposites with multimodal imaging capabilities of PAI, FL, and MRI would integrate various advantages to provide sensitive imaging of glioblastoma tumors at the early stage and compensate for the limitations of each imaging modality. In this study, we hope to provide an "all in one" strategy to fabricate a nanosystem that can be used for multimodal imaging guided photothermal therapy of GBM. We first synthesized a compound FTTBZ which can be employed for PAI and FL imaging. Then, we conjugate PEG-cRGD to this compound by click reaction to endow it with tumor targeting ability. FTTBZ-PEG-cRGD can self-assembly into nanoparticles in water, and its carboxyl group can chelate with Gd^{3+} for MRI. Beside, FTTBZ have a good photothermal effect, which can be utilized for photothermal therapy of GBM.

Publication List

None

Tailoring the Intrinsic Conductivity of Gold Nanoclusters Through Ligand Engineering for Electrocatalysis

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Abstract

Metal nanoclusters (NCs) with atomically precise composition and structure represent the forefront subclass of functional nanoparticles. They have broad application potential in the fields of catalysis, biomedicine, and sensing, etc. These broad applications are closely related to the structure of metal NCs, including metal cores, surface motifs, and protecting ligands. In particular, surface ligands can not only stabilize metal NCs in solution, but also provide them unique physicochemical properties for various applications. However, surface ligands composed of long hydrocarbon chains constitute an insulating barrier for metal NCs, which may have a negative impact on certain applications, such as reducing the mobility of charge carriers that require electrons to participate. In order to address this challenging issue, here, we use ligand engineering to design conductive metal NCs, and further explore their electrocatalytic performance. We have synthesized a series of Au NCs protected by different thiol ligands (e.g., 2-thiouracil-5-carboxylic acid (TCA) and para-mercaptobenzoic acid (pMBA)). Electrochemical studies have shown that the ligands with higher conjugation ability can improve the intrinsic conductivity of Au NCs. For example, Au-TCA NCs in which TCA has a heterocyclic ring containing N atoms, have the best electrochemical performance among the synthesized Au NCs. In particular, compared with Au-pMBA NCs (pMBA has a benzene ring), the conductivity of Au TCA NCs is increased by about 15 times, and the overpotential at 10 mA/cm2 for oxygen evolution reaction (OER) has been reduced by 90 mV. This metal NC with conjugated ligands has great potential in applications that require electrons to participate.

Publication List

1. **Z Liu**[#], Z Wu, Q Yao, Y Cao, O. J. H Chai[#], J Xie. Correlations between the fundamentals and applications of ultrasmall metal nanoclusters: Recent advances in catalysis and biomedical applications. *Nano Today.***2020**, 36,10153.
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Revealing the Structural Evolution of $(Ag/Au)_{44}SR_y$ Clusters Through the Intercluster Reaction between $[Ag_{44}(SR)_{30}]^{4-}$ and $[Au_{44}(SR)_{26}]^{2-}$

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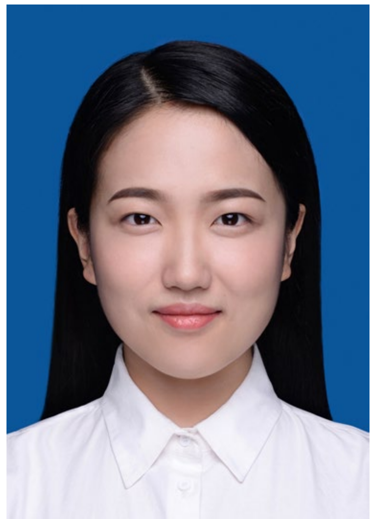
Abstract

Alloy chemistry can enrich the physical and chemical properties of metal nanomaterials. In particular, alloyed metal nanoclusters (NCs) with precise structures provide a powerful platform to study the structure/composition-related physical/chemical properties of metal nanomaterials at the atomic level. Recently, the continuous composition control of $Au_{25-x}Ag_xSR_{18}$ (x = 0-25, SR is a thiol ligand) has been achieved through different synthetic methods, such as co-reduction, hetero-metal salt or complex doping, and intercluster reactions. However, continuous composition control of relatively large metal NCs, such as $(Au/Ag)_{44}SR_y$, is still a challenge, since $Ag_{44}SRy_1$ and $Au_{44}SR_{y2}$ have different structures (e.g., the special mountain-like structure of the Ag_2SR_5 motif in $Ag_{44}SR_{30}$). Here, we developed an efficient and facile strategy to synthesize alloy $(Au/Ag)_{44}SR_y$ NCs, based on the reaction between $Ag_{44}SR_{30}$ and $Au_{44}SR_{26}$. The results show that by adjusting the ratio of A $Ag_{44}SR_{30}$ and $Au_{44}SR_{26}$ in the reaction, three sets of alloy NCs (i.e., $Ag_{44-x}Au_xSR_{30}$, $Ag_{44-x}Au_xSR_{27}$, $Ag_{44-x}Au_xSR_{26}$) have been successfully synthesized, where x is 1-12, 18-24, and 40-43, respectively. In addition, we used real-time electrospray ionization mass spectrometry (ESI-MS) to monitor the evolution of the main NCs products in the reaction, and performed a secondary reaction to study the relationship between these $(Ag/Au)_{44}SR_y$ NCs. This study provides new information for the intercluster reactions between NCs with the same number of metal atoms but different structures. In addition, the evolution of the final alloy NCs products can shed fundamental lights on the structure/composition-related physicochemical properties of the alloy $(Ag/Au)_{44}SR_y$ NCs.

Publication List

Lin, Y.; Cao, Y.; Yao, Q.; Chai, O. J. H.; Xie, J. Engineering noble metal nanomaterials for pollutant decomposition. *Ind. Eng. Chem. Res.* **2020**, 59, 20561–20581.

Strong Acid Functionalized Gold Nanoclusters for Enhanced Physicochemical Properties



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Abstract

Gold nanoclusters (Au NCs) are a subclass of gold nanoparticles with a diameter of less than 2 nm. The interesting molecular-like properties of Au NCs render them broad application prospects in the fields of bioimaging, sensing, and catalysis. In all these applications, the stability of Au NCs is the prerequisite. However, the weak ionization properties ofcarboxyl-thiol protecting ligands make Au NCs unstable in aqueous solutions, which limits their practical applications. To solve this problem, we propose a method to improve the stability of hydrophilic Au NCs by using strong-acid sulfonate-thiol ligands, such as para-mercaptobenzenesulfonic acid (p-MBSA). The strong ionization properties of p-MBSA can increase the surface charge of Au NCs unprecedentedly, thereby improving the stability of Au NCs in aqueous solutions. To confirm this hypothesis, we choose Au_{25} NC as the model system, and use para-mercaptobenzoic acid (p-MBA) as the representative of carboxyl-thiol ligands. The results show that the zeta potential of the as-synthesized $[Au_{25}(p\text{-}MBSA)_{18}]^-$ can reach –100 mV, which is in sharp contrast with $[Au_{25}(p\text{-}MBA)_{18}]^-$ (about –50 mV). The high surface charge density of $[Au_{25}(p\text{-}MBSA)_{18}]^-$ improves its stability in a wide pH range (pH = 3-10), high salt concentration (2 M NaCl), and high temperature (80 ℃). $Au_{25}(p\text{-}MBSA)_{18}$ with enhanced stability in solution can be used as an ultrastablenano-enzyme and can mimic the characteristics of peroxidase under acidic conditions (pH = 4–6). This study suggests that thiol ligands with a sulfonic group will become promising to protect and functionalize Au NCs for biomedical and catalytic applications.

Publication List

1. **Zhang, B.**; Wu, Z.; Cao, Y.; Yao, Q.; Xie, J., Ultrastable Hydrophilic Gold Nanoclusters Protected by Sulfonic Thiolate Ligands. *J. Phys. Chem. C* **2020**. accepted.
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Lanthanide-Doped All-Inorganic Halide Perovskites for Optoelectronic Applications

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Abstract

All-inorganic halide perovskite quantum dots$CsPbX_3$ (X=Cl, Br, I) have attracted considerable attention from both industrial and scientific communities since their birth in 2015, largely due to their tunable bandgapand high photoluminescence quantum yield. By taking advantage of quantum confinement effect at Bohr scale and large absorption cross-section, their emission can be tuned at any wavelength that fall into the full visible spectrum, along with high emission intensity. However, their application has been hampered by the shallow penetration of visible light. On that account, lanthanides are doped into perovskite hosts to achieve intrinsic NIR emission of trivalent rare earth ions. Serving as sensitizers, the perovskite hosts absorb excitation energy and efficiently transfer to lanthanides, enabling NIR emission with ultrawide spectrum even extending to NIR-Ⅱ window. Apart from enhanced emission intensity, an intriguing nonlinear optical phenomenon, namely quantum cutting, is also observed, showing 200% quantum yield theoretically.

The lead-related toxicity and easily decomposedcharacter are another two fatal weakness of halide perovskites,severely constraining their further blossom.As special subgroup among halide perovskites family, double perovskite single crystal $Cs_2(Ag_xNa_{1-x})(In_yBi_{1-y})X_6$ has been explored widely, benefited from their lead-free environmental friendliness, high stability, and large coordination number for heterogeneous doping. Resemble aforementioned quantum dots, lanthanides can also be alloyed into double perovskite single crystal for realizing NIR emission.

As a result, lanthanide-doped all-inorganic halide perovskites demonstrate great potential for optoelectronic applications such as NIR-emission LED, luminescent solar concentrator, and photovoltaic modules.

Publication List

None

Non-Radiative Energy Dissipation in Photoexcited Organic Charge Transfer Crystals

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Abstract

The research of excited state relaxation dynamics of organic crystals provides fundamentals for the exploration of photoluminescence and photothermal properties of organic materials, but also for the further development of several promising molecular based optoelectronic technologies, including photodetection, photovoltaic and light emitting. The one component organic crystals provide platforms for the research of the exited states with Frenkel excitons and the mixture of Frenkel and charge transfer excitons. The organic charge transfer crystals, which consist of two or more types of organic molecules, provide opportunities for the research of the relaxation of charge transfer excited state.

In this presentation, we report the recent development of charge transfer crystals and their optoelectronic applications. In particular, we show that non-radiative relaxation is usually dominant in the relaxation process of charge transfer crystals. Furthermore, by focusing on the properties of excitons and molecular vibrations in organic charge transfer crystals, the concept of diffusion and self-trapping of excitons and the vibrational modes of molecules are introduced to discuss the coupling between excitons and phonons. Finally, we make a conclusion on the non-radiative energy dissipation in photoexcited organic charge transfer crystals and describe some perspectives on the further development of organic charge transfer crystal based applications.

Publication List

None

All Inorganic Perovskite Based Direct X-ray Detectors

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Abstract

X-ray detection has been widely used in many fields, such as medical imaging, security check and nondestructive analysis.As an efficient approach to convert X-ray radiation directly into an electrical response, direct X-ray detection demonstrates a simple system configuration. Moreover, this direct detector literally has a higher spatial resolution than the indirect detectors due to the absence of optical cross talk among detector pixels.

In recent years, all inorganic halide perovskite has emerged as an excellent photoelectric material considering advantages of high carries mobility, high quantum efficiency and solution fabrication process. This material has also been found to exhibit high X-ray absorption owning to the component of heavy atoms (Cs, Pb, I, etc.). Hence the halide perovskite material has great potential to convert X-ray photons into electric signals efficiently. Nowadays, there are two popular approaches of the direct X-ray conversion: (1) singlecrystal-based devices; (2) polycrystalline devices. Compared with the polycrystalline film, the perovskite single crystal-based X-ray detector exhibits higher X-ray sensitivity and lowerdetection limit at lower electric fields. Therefore, we conclude that perovskite single crystal will be a promising material for direct X-ray detection.

Publication List

None

Stable Lithium Metal Anode Enabled by 3D Lithiophilic Current Collector

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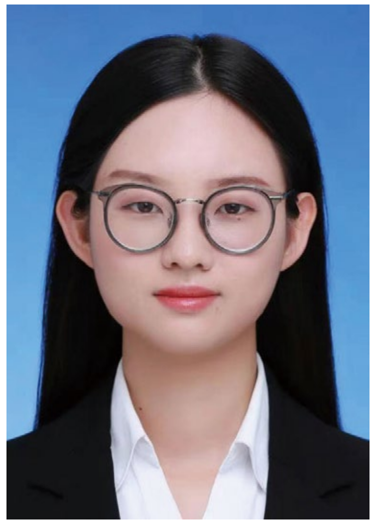
Abstract

Although the lithium (Li)-metal anode can deliver a high theoretical capacity of 3860 mAh g^{-1} at a low redox potential of -3.040 V (vs the standard hydrogen electrode), its application in rechargeable batteries is hindered by the poor Coulombic efficiency and safety issues caused by uncontrollable growth of Li dendrites and dramatic volume changes. To address this issue, designing 3D-structured current collectors is an effective strategy to facilitate rapid Li-ion flux and metal nucleation as well as mitigate Li dendrite formation through the kinetic control of metal deposition even at high local current densities. In this work, a 3D lithiophilic current collector for dendrite-free Li metal anodes is reported. The 3D lithiophilic current collector is demonstrated to be highly effective for promoting the uniform deposition of Li and suppressing the formation of dendrites. As a result, a Li metal anode based the above current collector has high coulombic efficiency (average 99.2% over 600 cycles at 1 mA cm^{-2}) and low overpotential (<10 mV at 1.0 mA cm^{-2}) during Li stripping/plating process.

Publication List

None

Covalent-Organic-Framework-Modified Zinc Anode for High-Performance Zn-ion Batteries



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Abstract

Recently years, aqueous Zinc-ion batteries (ZIBs) have attracted much attention due to their benefits of low cost, good compatibility, high volumetric capacity (5849 mAh g^{-1}), environment friendly, and so on. However, the drawbacks of Zinc dendrite growth and corrosion and the competitive hydrogen evolution deteriorate their electrochemical energy storage performance, thus designing and fabricating a stable electrolyte-Zn surface is much significant. Because of the merits of highly tunable porous structures with periodic ordered 1D channels, covalent organic frameworks (COFs) have been proved as potential ion conductors with good chemical and physical stabilities, including alkali metal ions as well as Zn ions. Here, a thin layer of covalent-organic-frameworks (COFs) is introduced as a protective layer for Zn foils, which aims to achieve a uniform and compact Zn deposition. A in situ growth method have been applied to explore a suitable COF layer for high-performance aqueous ZIBs. The preliminary results show that this modified strategy can improve the stability of Zn anode during the cycling.

Publication List

None

Single-Atom Electrocatalysts for Lithium Sulfur Batteries

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Abstract

Lithium sulfur (Li-S) batteries are considered as one of the most promising energy storage devices due to their high energy density, environmental friendliness and low cost. However, the practical applications of Li-S batteries have been hindered by the low utilization efficiency of sulfur aroused from complicated conversion process and the corrosion of Li metal electrode during charge/discharge process. Single atom catalysts (SACs) consisting of atomically-dispersed metal active sites have been recently exploited as high-performance electrocatalysts in diversity of energy storage devices including Li-S batteries due to their unique catalytic properties and maximized atom efficiency. Herein, we first identify the major roadblocks for the development of Li-S batteries. Following that, we will discuss the specific roles of various SACs in Li-S batteries including the cathode, separator, interlayer, electrolyte and anode, to reveal the detailed catalytic conversion mechanism of polysulfides and nucleation process of Li ions over single-atom active sites. In addition, the challenges and perspectives are proposed in order to accelerate the application of single atom materials in Li-S batteries.

Publication List

Wang, F.; Li, J.; Zhao, J.; Yang, Y.; Su, C.; Zhong, Y. L.; Yang, Q.-H.; Lu, J., Single-Atom Electrocatalysts for Lithium Sulfur Batteries: Progress, Opportunities, and Challenges. *ACS Materials Letters* **2020**, 1450-1463.

3D Carbon as Inorganic Filler Toward Stable Composite Solid-state Electrolyte for All Solid-State Li Metal Battery

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Abstract

All-solid-state Li-metal batteries are widely explored since their superior safety and potential high energy density. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in Poly(ethylene oxide) (PEO) composite is one of the outstanding solid-state electrolytes because of its acceptable voltage windowand good film-forming property. However, the low ionic conductivity of PEO-LiTFSI electrolyte at room temperature (RT) (10^{-6}-10^{-5} S/cm), poor mechanical property and inferior long range cyclic stability limit its practical application. Here, three-dimensional (3D) carbon which with high surface area was prepared with using facile salt-assisted method and used as inorganic filler of PEO-LiTFSI electrolyte. The Li+ ionic conductivity is improved to two times at RT with a small amount of 3D carbon addition. In addition, the composite electrolyte shows good stability against Li metal at 0.1, 0.2, and 0.3 mA cm^{-2} at 60 ℃ compared with pure PEO-LiTFSI. Moreover, $LiFePO_4$|PEO+LiTFSI+carbon|Li battery displays enhanced stability toward different rate charge and discharge processes.

Publication List

None

A Unique Electrolyte Additive for the Improved Electrochemical Performance of Li-O_2 Batteries

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Abstract

The studies of organometallic redox mediators (organometallic RMs) are relatively few and do not exhibit significantly satisfying performance, compared to other types of RMs. Meanwhile, the organometallic RMs mainly focus on Fe^{2+} or Co^{2+}-containing RMs while RMs containing other central metal ions are ignored to study. In view of these present situations and plus that the failure reason of organometallic RMs is not studies in depth, manganese acetylacetonate ($Mn(acac)_3$) is chosen in this paper due to the abundant content of manganese in earth and fabulous catalytic performance. By doing electrochemical test, it is found that $Mn(acac)_3$ as an effective redox mediator can not only reduce charge overpotential of Li-O_2 batteries according to the galvanostatic charge/discharge test, but also enhance the stability towards lithium metal anode based on the results of symmetric batteries.

Publication List

Cui, X. H.; **Luo, Y. N.**; Zhou, Yin. Dong, W.H.; Chen, W. Application of Functionalized Graphene in Li-O_2 Batteries. *Nanotechnology*. **2020**. https://doi.org/10.1088/1361-6528/abd1a7 (co-1st author)

Atomically Dispersed Ni-N-C Decorated with Pt toward Hydrogen Evolution Reaction

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Abstract

Hydrogen evolution reaction (HER) is a vital process to produce H_2 as fuel by water splitting, whereas electrocatalyst plays a dominant role in determining reaction kinetics. Designing electrocatalyst with high catalytic activity and low cost is crucial to replace the noble metal catalysts. Here we report a composite HER catalyst consisting of Pt attached to a N-doped carbon substrate with atomically dispersed Ni-NC sites, which was synthesized with atomic layer deposition (ALD) technique. The PtNi-NC exhibits enhanced catalytic activity and durability, with overpotential of 30 mV for HER in acidic media at a current density of 10 mA cm^{-2}, comparable with commercial 20wt% Pt/C. HAADF-STEM and XANES were conducted to elucidate origin of the enhanced catalytic properties.

Publication List

Da, Y. M.; Li, X. P.; Zhong, C.; Deng, Y. D.; Han, X. P.; Hu, W. B. Advanced Characterization Techniques for Identifying the Key Active Sites of Gas-Involved Electrocatalysts. *Adv. Funct. Mater.* **2020**, 30, 2001704.

MOF-based Material for Electrocatalytic Application

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Abstract

High-performance electrocatalysts are key in many energy conversion and storage systems. Presently used catalysts for the oxygen evolution reaction—a reaction central to metal–air batteries and water splitting technologies—typically require noble metal oxides, which are costly. Furthermore, large overpotentials to drive the reaction decrease the energy conversion efficiency and hinder the practical application of devices.

MOFs are formed by coordination bonds between organic ligands and metal atom nodes with periodic structural units. Due to their structural characteristics, MOFs could provide the inherent advantages of both homogeneous and heterogeneous catalysts. Analogously to molecular catalysts, nano-dimensional porous MOFs possess well-defined chemical structures and readily accessible active sites. Also, MOFs are highly crystalline solid materials, which are conveniently recyclable and robust under both chemical and physical attack. Thin-film electrodes based on MOFs have exhibited promising electrocatalytic activity towards water oxidation.

The utilization of MOFs is classified based on three aspects. Firstly, MOFs serve as sacrificial templates for the synthesis of metal oxides by the removal of organic linkers after calcination. Secondly, MOFs act as precursors for nitrogen-doping carbon by the pyrolysis process, which inherits the porosity of original MOFs. Thirdly, pristine MOFs can be directly employed as electrode materials. MOFs can be potential candidates as electrode materials because of their merits, such as huge surface area and tunable pore distribution, which are required for good electrochemical performance.

Here, we report ultrathin MOF derivatives as electrocatalysts for OER and HER. Our bimetal–organic framework derivatives show good electrocatalytic performances.

Publication List

None

Gas Phase Salt Assisted Synthesis Advanced 2D Materials

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Abstract

Since graphene was discovered, 2D material family keep growing. Recently, abundant polynary 2D materials were discovered and showed fantastic properties in electronic device, but the fabrication process is complex and it's very hard to control. Traditional CVD routine is used to synthesis those 2D materials, but it takes too much time and is very hard to control the thickness. Salt, which is cheap and safe, can play a very important role in novel 2D materials fabrication. Thus, using salt to adjust and optimize the synthesis of polynary 2D materials is proposed and we are trying to figure out the potential role salt plays in this routine.

Publication List

None

In-situ Spectroscopy Investigation of Alkali Metal Interaction Mechanism with Organic Semiconductor for Li-Anode

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Abstract

In order to develop LIBs with higher energy density, improvement for anode materials is indispensable. And using organic anode materials is a novel and promising strategy, owing to their redox reaction mechanism and tunable property. However, because of the intrinsic low conductivity of the organic materials, they are usually mixed with carbon additives to form as the anode and work in the electrochemical property test in recent studies. In this way, it is hard to understand the real interaction process between organic materials and alkali metals and their contribution to the electrochemical performance. Moreover, in order to design and synthesize anode materials with higher capacity, understanding the lithium storage mechanisms of different functional groups is also really significant. Therefore, I focus on in-situ spectroscopy investigation of the alkali metal interaction mechanism with organic semiconductor for Li-anode. With better understanding of the interaction mechanisms, it will be more efficient to explore and design promising organic anode materials and batteries with higher capacity. For my first work, sexiphenyl and pentacene were chosen and the chemical and electronic structure evolutions upon the deposition of lithium (Li) on them have been investigated by in-situ x-ray photoemission spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). The interactions of them with sodium and potassium are also studied, since sodium ion batteries and potassium ion batteries are thought to be promising next-generation batteries recently.

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Chemical Looping Oxidative Dehydrogenation of Propane on Redox Catalysts

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Abstract

Propene is and will remain the essential pillar of chemical and petrochemical industry because it is vital intermediate to produce a series of chemicals, including polypropylene, propylene oxide, cumene, acrylic acid and isopropanol etc. With the rising and sustained use of downstream chemicals and low-efficient propene production, the gap between propene supply and demand is gradually increasing. Chemical looping technologies afford a promising platform that utilizes metal oxides as oxygen carriers for economic and effective propene processing. In principle, chemical looping oxidative dehydrogenation of propane (CL-ODHP) enables the process decomposed into dehydrogenation and regeneration reactions via chemical intermediates (namely oxygen carriers), which are reduced and regenerated individually and periodically. This unique redox process hinges critically on the properties of metal oxides such as oxygen storage capability, crystal structures, ionic transport ability, redox mechanism, and reaction kinetics. Hence, it is imperative to investigate the cyclic redox schemes and establish convincing structure-performance relationship to guide the rational design of redox catalysts for CL-ODHP process.

Publication List

None

Genetic Algorithm for Global Structure Optimization of Catalytic SurfaceSystem

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Abstract

For a catalytic system, understanding the global minima (GMs) is significant for predicting the stable structures of catalysts, analyzing the adsorption behavior of catalysts, studying the mechanism of heterogeneous reactions, constructing reaction pathways, and so on. However, limited by current characterization techniques, it is very expensive and difficult to directly observe the GMs through experiments. A global optimization algorithm from a theoretical perspective is needed to efficiently search the GMs within a reasonable time.

The genetic algorithm (GA) is a search technique based on the principles of natural evolution. It uses operators that are analogs of the evolutionary processes of crossover, mutation, and natural selection to explore PES. With a strong global search capability, GA is especially suitable for the optimization problems that have no prior knowledge of the GMs.

Currently, we already developed a parallel, multi-population GA using Python language, for global structure optimization of supported catalyst. With the help of efficient sampling method, uncertainty measurements archived by Gaussian process regression and active learning framework, our GA program could preliminarily work in structure with tens of atoms, and could find low-lying structure of surface catalytic system like surface oxygen on Pt(111).

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Energy Conversion for CO_2 Hydrogenation and H_2 Production

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Abstract

With the increasing of industrial development, greenhouse effect and energy shortage become more and more severe, most fossil fuels were directly consumed. However, the associated increase in anthropogenic carbon dioxide (CO_2) emissions may have a negative effect on global temperatures, ocean acidity as well as ecological issues. Therefore, one of the promising approaches in this regard is converting CO_2 into value-added chemical and fuels by using renewable energy. Such energy-efficient conversion by CO_2-based feed not only can alleviate CO_2 emission but also minimize the environmental issues caused by depletion of fossil fuels. On the other hand, other strategy is Hydrogen production which can replace fossil fuels due to its clean production (H_2O) and high combustion value. Hence, we focus on the synthesis of high-efficiency catalyst with high catalytic ability, high selectivity as well as high stability by using different method in CO_2 conversion and H_2 production. Furthermore, we also investigated the reaction mechanism to explore the relationship of structure-function effect.

Publication List

None

Promoting Photocatalytic Formic Acid Decomposition via Transient Illumination

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Abstract

Photocatalytic hydrogen production is an attractive approach to convert light into clean and renewable fuels. Most photocatalytic systems for this application involved semiconductor material and sacrificial hole scavenger to avoid electron-hole recombination. Noble metal promoted TiO_2 photocatalysts were extensively studied due to improved separations of charge carriers and surface charge transfer reactions. Although precise design of the photocatalysts is vital in optimizing this reaction, the overall catalytic activity is still limited by the Sabatier principle. Hence, inspired by catalytic resonance theory, transient illumination was implemented to potentially overcome the Sabatier volcano for photodecomposition of hydrogen storage chemicals to generate H_2.

In this study, photodecomposition of formic acid was selected as model reaction over Pt/TiO_2. Preliminary experimental results suggest that the highest quantum yield achieved at transient illumination was approximately 3 times higher when compared to that of static illumination. Further investigations were implemented to gain insights on the mechanisms that contribute to the observed photocatalytic promotion for this reaction.

Publication List

Wong, S.S.; Shu, R.; Zhang, J.; Liu, H.; Yan, N. *Chem. Soc. Rev.* **2020**, 49 (15), 5510

Using N_2 as a Feedstock for Organonitrogen Chemicals

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Abstract

Organonitrogen chemicals find wide applications in pharmaceutical industry, agriculture, textile and other polymer industries, and beyond. At present, ammonia is dominantly used as a nitrogen source to construct nitrogen-containing functional groups in most synthetic paths. Unfortunately, ammonia synthesis (Haber-Bosch process) conditions are harsh and the process is inefficient. It is estimated that annual energy consumption accounts for about 2% of global energy. Develop catalytic systems that are able to directly use nitrogen gas to access organonitrogen compounds represents an ultimate solution bypassing the Haber-Bosch process.

Inspired by the chemical looping process for ammonia synthesis based on alkali and alkaline earth metal imides as nitrogen carriers under mild conditions, we proposed a strategy to establish a pathway to convert nitrogen gas to functionalize nitrogen-free organic compounds in a continuous flow system, using LiH and Ru-based catalyst under relatively mild conditions. Preliminary results suggest that while N_2 has been effectively fixed in the form of $LiNH_2$, further conversion of $LiNH_2$ into organonitrogen compounds is not easy due to severe side reactions induced by strongly nucleophilic species in NH_2^-.

In parallel, we intend to develop an integrated system to sequentially convert nitrogen gas first into ammonia and then into nitrogen-containing functional groups in a batch reactor using a “cocktail” catalyst. In the first stage, we aim to realize nitrogen activation in the presence of hydrogen. The as-prepared $Ru\text{-}Cs/r\text{-}CeO_2$ catalyst reached ammonia productivity of 32 $\mu mol/g_{cat}/h$ in nitrogen activation under 573 K and 2MPa (N_2 :H_2=1:1) pressure. In the second stage, we expect that the generated ammonia can be introduced in situ into organic compounds.

Publication List

Li H.; Yan N. *Chem.* **2020**, 6, 2871-2873.

Methane Conversion Into Value-Added Organic Chemicals

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Abstract

Methane is a widely-distributed green energy source and an important building block for various value-added organic chemicals, but the methane molecule is rather stable and hard to be activated and converted into aim organic products. Among various methane conversion approaches, partial oxidation of methane (POM) to methanol at low temperature and methane pyrolysis at high temperature are two promising routes.

For POM process, multiple homogeneous/heterogeneous catalytic systems have been proposed, such as Periana-Catalytica Systems, AuPd-based catalysts and Rh/ZSM-5. Nonetheless, preventing deep oxidation of oxygenated products without compromising C-H activation remains a challenge. To explore improved heterogeneous catalysts for POM, we first developed an aqueous Pd@Pt core-shell colloidal catalyst, which can realise a direct methane conversion to CH_3OH and CH_3OOH using H_2O_2 at 50°C with high selectivity (up to 92.4%) and good productivity (up to 89.3 mmol g $Pd@Pt^{-1}$ h^{-1}).

For methane pyrolysis, the dilemma of conversion and selectivity of certain hydrocarbon products has restricted the development of direct methane conversion for a long time. Here, we designed a novel non-isothermal filament reactor for high-temperature methane conversion into certain products with enhanced productivity. The methane conversion is aimed to be promoted by the high temperature on the filament, while the selectivity is expected to be improved by the catalyst at lower temperature zone.

Publication List

None

CO_2 Hydrogenation to Methanol based on Zr-MOF Catalyst

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Abstract

The capture and conversion of CO_2 have been widely studied by a group of scientists with the increasing level of CO_2 resulting in the global warming. Cu-based catalysts are popular for directly conversion of CO_2 to methanol because of the high activity and low cost. Metal organic frameworks (MOFs) with extraordinarily large surface area and a well-defined porosity is a good option for catalysts. Based on that, this work mainly focusses on the preparation of Cu-Zr-based catalysts by pyrolysis of Zr-MOF, MOF-808, for CO_2 hydrogenation to methanol. Firstly, MOF-808 was modified by L-histidine to create the site for coordination with $Cu^{2+,}$ then high temperature pyrolysis can promote the creation of interface of Cu and ZrO_2. The strong metal-support interaction (SMSI) at Cu-ZrO_2 interface can be adjusted by different calcination temperature to control the catalytic performance for CO_2 hydrogenation. In addition, the reaction of CO_2 hydrogenation to methanol can happen at low temperature, 150°C with 100% selectivity. The work is significant for the design of Cu-based catalyst for CO_2 hydrogenation.

Publication List

None

Carbon Capture and Low-Temperature Conversion Using Metal–Organic Frameworks

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Abstract

Rapidly increasing atmospheric CO_2 concentrations threaten human society, the natural environment, and the synergy between the two. In order to ameliorate the CO_2 problem, carbon capture and conversion techniques have been proposed. Metal–organic framework (MOF)-based materials, a relatively new class of porous materials with unique structural features, high surface areas, chemical tunability and stability, have been extensively studied with respect to their applicability to such techniques. Recently, it has become apparent that the CO_2 capture capabilities of MOF-based materials significantly boost their potential toward CO_2 conversion. MOFs have high CO_2 adsorption capacities and adjustable pore apertures and cavities. Many of the same active sites applied to CO_2 capture, including OMSs or LASs, Brønsted acid sites (BASs) and LBSs, can convert CO_2 into chemical products by organic transformation. This is frequently analogous to the transformations performed by numerous conventional homogeneous and heterogeneous catalysts. The utilization of MOFs' intrinsic functionalities for CO_2–epoxide cycloaddition reactions has been widely explored. This class of reactions can yield products with a variety of applications. Specifically, cyclic carbonates, the major product of many CO_2 cycloaddition reactions, have been widely applied as intermediates for the production of engineering plastics, electrolyte solvents for lithium-ion batteries, polar aprotic solvents, degreasers, and fuel additives.

Publication List

None

The Relationship Between Catalytic Performance and the Active Site Structure for Single-Atom Catalysts

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Abstract

Single-atom catalysts (SACs) have attracted tremendous amount of interest lately. Our lab has developed a strategy to stabilize Pd single atoms on polyoxometalates (POMs) and used for the hydrodeoxygenation of acetophenone as a model compound. Pd/Cs-Phosphotungstic acid (PTA) exhibited excellent activity and selectivity for ethylbenzene. But Pd^0 tend to aggregate on Pd/CsPTA surface during HDO reaction due to the high surface energy of Pd^0. Thus, my project is to stabilize the Pd^0 on Pd/CsPTA by different strategy. Firstly, we intend to separate the Pd/CsPTA by Silomolybdic acid (SMA) so that prevent the movement of Pd^0. Furthermore, we expect more different catalytic properties after the introduction of SMA to Pd/CsPTA. For the hydroformylation of olefins, homogeneous catalysts generally possess superior catalytic performance compared to heterogeneous catalysts. However, the issue of catalyst separation and recycling severely limits their use in practice applications. SACs have the advantages of both homogeneous catalysts, such as isolated sites, and heterogeneous catalysts, such as stability and reusability, and thus would be a promising alternative to traditional homogeneous catalysts. Thus, we prepared Rh SACs supported on CeO_2 catalyst, which demonstrate similar efficiency compared to that of homogeneous Wilkinson's catalyst. Infrared CO chemisorption experiments identified isolated Rh atoms on the support.

Publication List

None

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