天津大学
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2nd NUS–TJU PhD Online Workshop

8th–9th Jan 2022

天津大学-新加坡国立大学
福州联合学院

2nd 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 second in its series taking place online in January 2022. 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.

2022 Workshop Organizing Committee (Students):
Fan Renzhen, Zhang Boyi, Lin Zhikeng, Luo Xiaohua, Zhang Bihan, Lin Yingzheng,Wang Meng, Yang Haotian, Chang Jinquan, An Hua

2022 Workshop Organizing Committee (PIs):
Chen Wei, Geng Yanhou, Xie Jianping, Yan Ning, Zhao Yu

catalogue

Workshop Schedule

NUS-TJU PhD OnlineWorkshop, 8th-9th Jan 2022

Center 1: Optoelectronics Symposium Chair:

Fan Renzhen, Zhang Boyi

NUS-TJU PhD OnlineWorkshop, 8th Jan 2022

Center 1: Optoelectronics Symposium Chair: Fan Renzhen

		Presenter	Title	Supervisor
Session Chair: Fan Renzhen				
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 2D 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: Fan Renzhen			
	11:00-11:20	Yang Hao	Designed Synthesis of Novel Covalent Organic Frameworks	Jiang Donglin
	11:20-11:40	Pu Guiqiang	New Mechanisms and Applications for Organic-Inorganic Hybrid Lanthanides-Doped Nanosystem	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: Fan Renzhen				
Afternoon	14:00-14:20	An Chuanbin	Highly Stretchable and Elastic Polymer Semiconductors Based on Polyurethane Multiblock Copolymers	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 Isoindigo- and Thienoisoindigo-quinoids for organic field effect transistors （OFETs）	Geng Yanhou & Chi Chunyan
	15:00-15:20	Zhang Qing	Controllable preparation of two-dimensional van der Waals heterojunctions for high-performance optoelectronic devices	Hu Wenping & Chen Wei
	15:20-15:30: Break			
	Session Chair: Fan Renzhen			
	15:30-15:50	Wang Congyong	Metal Halide Perovskite/Organic Semiconductor-based Field-Effect Transistors	Hu Wenping & Wu Jishan
	15:50-16:20	Zhu Xiaoting	Negative phototransistors with ultrahigh sensitivity and weak-light detection based on 1D/2D molecular crystal heterojunctions	Hu Wenping & Wu Jishan
	16:20-16:40	Zhou Qifeng	Synthesis of belt-shaped fully fused carbon nanostructures	Wu Jishan
	16:40-17:00	Xin Shan	The Aromaticity of expanded radialenes and its charged species	Wu Jishan
	17:00-17:20	Zhang Qiuyu	Property Study of Polyradicaloids Systems	Wu Jishan

NUS-TJU PhD OnlineWorkshop, 9th Jan 2022

Center 1: Optoelectronics Symposium Chair: Zhang Boyi

		Presenter	Title	Supervisor
Session Chair: Zhang Boyi				
Morning	9:00-9:20	He Weixin	Two-Dimensional Ferroelectric Dion-Jacobson Perovskite	Loh Kian Ping & Chen Wei
	9:20-9:40	Zheng Haining	Design and Synthesis of Two-Dimensional Ferroic Hybrid Perovskites	Loh Kian Ping
	9:40-10:00	Zhu Youhuan	Stabilization of 3D $K_{0.2}Na_{1.3}Mn_{0.5}O_2$ via K doping for high efficiency oxygen redox	Loh Kian Ping
	10:00-10:20	Ye Xingyao	Covalent Organic Frameworks for photo- and enzyme tandem catalysis	Jiang Donglin
	10:20-10:40	Deng Lejian	Synthesis and Function of Covalent Organic Framework Crystallites	Jiang Donglin
	10:40-11:00: Break			
	Session Chair: Zhang Boyi			
	11:00-11:20	Ding Zhichao	Design and Functions of Conductive Covalent Organic Frameworks	Jiang Donglin
	11:20-11:40	Xu Duo	Study on Stimulus-responsive Room-temperature Phosphorescent Materials	Li Zhen & Liu Xiaogang
	11:40-12:00	Jiang Wanqing	Stable luminescent radicals applied in optoelectronic applications with doublet emission	Li Zhen & Wu Jishan
	12:00-12:20	Cao Yalei	Design and synthesis of AIE organic functional materials with chemiluminescence for biological applications	Li Zhen & Liu bin
Lunch Break				

		Presenter	**Title**	**Supervisor**
Session Chair: Zhang Boyi				
Afternoon	14:00-14:20	Fan Renzhen	Convergent synthesis of oligothiophene-based quinoidal compounds and their properties	Geng Yanhou & Chi Chunyan
	14:20-14:40	Shi Kaimin	Synthesis and characterization of conjugated materials based on isoindigo derivatives	Geng Yanhou & Wu Jishan
	14:40-15:00	Chen Xiaofeng	Thiophene-based Ladder-type molecules for High-performance Conjugated Organic Semiconductors	Geng Yanhou & Wu Jishan
	15:00-15:20	Zhang Jing	Fluorescent Lateral-Flow Immunoassays for Thrombus-marker Detection	Hu Wenping & Liu Bin
	15:20-15:40	Shi Zhuojie	Imide-based electron transport materials for perovskite solar cell	Hu Wenping & Hou Yi
	15:40-16:00: Break			
	Session Chair: Zhang Boyi			
	16:00-16:20	Xiong XinCheng	Polymeric Field-effect Transistors Achieved by Solution Methods and Understanding of Morphology-Performance Relationships	Hu Wenping & Chua Lay-Lay
	16:20-16:40	Zhang Boyi	The Synthesis of Graphyne Wheel	Wu Jishan
	16:40-17:00	Shen Tong	Solution-processed Nanographenes for NIR Laser Materials	Wu Jishan
	17:00-17:20	Sun Zhitao	Zethrene-based diradicaloids	Wu Jishan

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 carbon plates for the immobilization of SACs to enhance catalytic activity and stability. Our carbon-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 carbon-based SAC, together with its reusability and scalability, renders it promising for industrial productions.

Publication List

1. 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.* Iron Single Atom Catalyzed Quinoline Synthesis. *Adv. Mater.* **2021**, 33, 2101382
2. **Song, J.#**; Chen, Z.#; Cai, X.#; Zhou, X.; Zhan, G.; Wei P.; Yan, N.; Xi, S.* and Loh, K. P.* Corporative Activation of Nitrile-Azide Cycloaddition in a High-Loading Cu1-C3N4 Single Atom Catalyst. *Manuscript under review.*
3. Chen, Z.#; **Song, J.#**; Zhang, R.#; Hu, Q.; Li, R.; Wei, P.; Xi, S.; Zhou, X.; Phuc, N. T. T.; Minh, D. H.; Lee, P. S.; Zhao, X.; Koo, M. J.; Yan, N. and Loh, K. P.* Addressing the Quantitative Conversion Bottleneck in Single-Atom Catalysis. *Manuscript under review.*

Metallo 2D covalent organic frameworks

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Abstract

The discovery of graphene has inspired great efforts devoted to organic 2D materials (organic two-dimensional materials) because of their highly accessible active sites on surfaces and highly diversity of organic building blocks. These organic building blocks can be connected by coordination bonds or covalent bonds, which refer to 2D MOFs (2D metal-organic frameworks) and 2D COFs (2D covalent organic frameworks), respectively. Compared with 2D COFs, the combination of metal ions and organic linkers of 2D MOFs renders them sophisticated functionalities. However, the strong covalent bonds of 2D COFs render them better stability than 2D MOFs, which benefit them in practical use. To combine sophisticated functionalities of 2D MOFs and the stability of 2D COFs, a kind of new material, metallo 2D COF, was created. So far, research on metallo 2D COF has been mostly restricted to the limited library of organic building blocks, such as bidentate building block (2,2’-bipyridine) and tetradentate building blocks (salen, porphyrin, and phthalocyanine). Here, a half-open building block, pyridine-2,6-diimines was firstly introduced into metallo 2D COFs, which enriched the library of metallo 2D COF.

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 have changed with the ratio of Se in the MoSeO from thin flakes to thicker products with color changes under optical microscopy. Energy dispersive X-ray spectroscopy (EDS) shows the ratio of Mo/Se in the MoO_xSe_y is between 0 and 1.15. The new peak at 25.8° in X-ray diffraction (XRD) patterns indicate the formation of MoSeO. The measurements of transport property of MoO_xSe_y turn 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 and becomes significant when the Se/Mo ratio increases to 1.15. These results indicate MoOxSey 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, background, 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.1

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

1. 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**, 50, 120-242.
2. Jin, E.;+ Geng, K.; + Fu, S.; + Addicoat, M.; Zheng, W.; **Xie, S.**; Hu, Jun.; Hou,X.; Wu, X.; Jiang, Q.; Xu, Q.; Wang, H.; Jiang, D. Module-Patterned Polymerization towards Crystalline 2D sp2-Carbon Covalent Organic Framework Semiconductors. Angew. Chem., Int. Ed. **2021**, 10.1002/ange.202115020

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.

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

1. Covalent Organic Frameworks: An Ideal Platform for Designing Ordered Materials and Advanced Applications. Ruoyang Liu, Ke Tian Tan, Yifan Gong, Yongzhi Chen, Zhuoer Li, Shuailei Xie, Ting He, Zhen Lu, **Hao Yang**, and Donglin Jiang*. Chem. Soc. Rev., **2021**, 50, 120—242.

New Mechanisms and Applications for Organic-Inorganic Hybrid Lanthanides-Doped Nanosystem

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Abstract

The organic-inorganic hybrid strategy shows unique photophysical properties and wider applications in lanthanides doped nanosystems (LDNCs). Organic ligands and nanocrystals can complement each other in light capture, energy transfer and specific emission, which is obviously better than that of single component. Based on the above hybrid strategy, we main focus on the following two works. In the first work, given the energy conversion ability of hybrid organic-inorganic nanomaterials is always severely weakened upon introduced into solid optoelectronic devices. We designed a novel triphenylamine-benzobisthiadiazole derivative (TBC) that displays excellent aggregation induced emission (AIE) characteristics to assist LDNCs in terms of excellent energy conversion ability from ultraviolet-visible to near-infrared region in solid polymer film. The sensitization efficiency of TBC to LDNCs in solid film could be dramatically enlarged to 64.8 % compared with 51% in solution. This finding that combines AIE molecules with inorganic nanocrystals could provide a new way for building solid optoelectronic devices with efficient energy transfer efficiency. In the second work, considering the maximum lifetime of conventional upconversion luminescence (UCL) can only reach to hundreds of microseconds, which is not conducive to time-resolved applications. We proposed the UCL with ultralong lifetime up to 1.3 s via organic-inorganic hybrid strategy. Polymeric PSSH, that exhibits strong triplet state emission under ambient conditions, is anchored to the surface of LDNCs, and long-lived UCL is feasible by transferring upconverted energy from LDNCs to PSSH after NIR laser excitation. Time resolved applications could be developed based on proposed ultralong-lived UCL system.

Publication List

None

The Derivatives of Triphenylaminewith Room Temperature Phosphorescence

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Abstract

Organic room temperature phosphorescent materials are known for their synthetic feasibility, tunable phosphorescence wavelength and long lifetime, etc. Among those, triphenylamine derivatives are phosphorescence active due to the presence of nitrogen atom, donor-acceptor (D-A) structure and intermolecular interactions in the crystal state. Here we have synthesized varied triphenylamine derivatives with various functional groups, such as 4-(diphenylamino) benzoic acid (TPA), 4-Phenothiazin-10-yl-benzoic acid, 4-(10H-phenoxazin-10-yl)benzoic acid, 4-(diphenylamino)benzoic acid methyl ester and so on, following by the fabrication of doped films and the study of the room temperature phosphorescence (RTP) of these materials. Detailed studies are carried out to investigate the relationship between the phosphorescence and respective functional group modification. The longest afterglow at room temperature in air of TPA@PVA doped film without NH3 • H2O has been achieved by the interplay of strong intermolecular interactions, efficient intersystem crossing using functional group variation and the reaction between organic molecules and films. In addition, during five circles of fuming and heating, there was the light-responsive and heating-responsive RTP observed, and ester bonds appeared, resulting in the enhanced RTP during circles. What is more, the emission maybe packing-dependent, so it is necessary to analyze their optical properties, intermolecular interactions and crystal structures in these triphenylamine derivatives, which can guide the reasonable design of organic molecules with special light-emission properties.

Publication List

Tian, Z.; Han C.; **Zhao Y**.; Dai W.; Lian X.; Wang Y.; Zheng Y.; Shi Y.; Pan X.; Huang Z.; Li H.; Chen W., Efficient photocatalytic hydrogen peroxide generation coupled with selective benzylamine oxidation over defective ZrS3 nanobelts. Nat. Commun. 2021, 12, 2039. https://doi.org/10.1038/s41467-021-22394-8

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

Highly Stretchable and Elastic Polymer Semiconductors Based on Polyurethane Multiblock Copolymers

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Abstract

Polymer semiconductors with large elastic recovery (ER) under strains are highly desirable for stretchable electronics. In this work, multiblock copolymers based on PBTTT with excellent mechanical properties have been successfully synthesized. Based on this, we have successfully obtained truly stretchable semiconductors with both good elasticity and stretchability using the method of physical blending. In terms of stretchability, the breaking strain of the freestanding blend 1:3 film reached 200% and *COS* of blend 1:3 film was higher than 300%; In terms of elasticity, the elastic recovery was higher than 80% under all strains tested; In terms of electrical property, the mobility of blend 1:3 is almost the same as those of PBTTT homopolymer reported in many papers. At the same time, the electrical property can be maintained when the film was stretched 1000 times under 50% and 100% strain. These features showed that the method of preparing multiblock copolymer and combining physical blending is an effective strategy for preparing stretchable semiconductors. It should be pointed out that the versatility of this new strategy has yet to be verified. The entire molecular design of rod-coil polyurethane multiblock copolymers and physical blending are based on PBTTT, a typical polymer with high crystallinity. Further research is therefore needed to extend molecular design strategy to other types of conjugated polymers to obtain more thermodynamically and mechanically stable, stretchable and elastic semiconductors.

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. Thieno[3,4-b]thiophene (TbT) displays intrinsic chemical stability as a result of the quinoid-enhancing character. 1,3-indandione-terminated quinoids with the different number of TbT cores are designed and successfully synthesized. The influence of the quinoidal conjugation length on the photophysical, electrical properties and stability have been systematically investigated. On the base of the previous investigation, thieno[3,4-c]pyrrole-4,6(5H)-dione unit was introduced into the backbone of 1,3-indandione-terminated quinoidal TbT in order to further decrease the LUMO energy levels. In addition, fluorinated 1,3-indandione was also troduced to accurately tune the energy levels. The synthesis of them is currently underway.

Publication List

None

π-conjugated Isoindigo-and Thienoisoindigo-quinoids for organic field effect transistors（OFETs）

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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), a large number of studies on the materials design have been undergoing. Herein, π-conjugated materials with quinoidal structure like isoindigo-based OSCs have been evaluated as a good potential semiconductor material for OFETs. Herein, isoindigo-derivatives instructed with other conjugated structure (benzo[1,2-b:4,5-b']difuran-2,6(3H,7H)-dione) as a new building block substituted with cyanoquinomethane termini and large fused ring will be studied and prepared OFETs to explore the relative properties.

Publication List

None

Controllable preparation of two-dimensional van der Waals heterojunctions for high-performance optoelectronic devices

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Abstract

Two-dimensional (2D) materials have attracted numerous attentions in past few decades due to their superior and intriguing optoelectronic properties. With the increasing demand for multifunctional applications, van der Waals (vdW) heterojunctions based on 2D materials have also been involved in the construction of optoelectronic devices because the integration of distinct 2D materials can effectively broaden their physiochemical properties, create novel device architectures, and/or create new functionalities of the existing 2D vdW materials without considerations of lattice matching in highly disparate material systems. However, the controllable preparation of high-performance 2D vdW heterojunctions still remains a challenge. Three major concerns are involved regarding the development of 2D vdW heterojunctions: large-area integration, exploration of interface charge transport at the 2D limit and advanced functional device applications. Here we design a serious of 2D vdW heterojunctions manufactured *via* space-confined drop-casting, aiming to fulfill the demand for large-area integration. TMDs, MXenes, and metal oxides are inorganic options for heterojunction preparation in our research, whereas poly(3-hexylthiophene-2,5-diyl) (P3HT), Poly{3,6-dithiophen-2-yl-2,5-di(2-decyltetradecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-alt-thienylenevinylene-2,5-yl} (PDVT-10), and other organic materials are also involved. On this basis, a variety of advanced devices, such as artificial photonic synapses, phototransistors with ambipolar photoresponse and vertical field effect transistors, can be produced, further allowing for more in-depth research into the mechanism of interfacial charge transfer.

Publication List

1. **Zhang, Q.**; Jin, T.; Ye, X.; Geng, D.; Chen, W.; Hu, W. *Adv. Funct. Mater.* **2021**, 31, 2106151.
2. **Zhang, Q.**; Ye, X.; Zheng, Y.; Wang, Y.; Li, L.; Gao, Z.; Wu, J.; Dong, H.; Geng, D.; Hu, W. *J. Mater. Chem. C* **2021**, DOI: 10.1039/D1TC02284A.
3. Fan, Y.; Li, M.; Jia, X.; Li, L.; **Zhang, Q.**; Gao, E.; Geng, D.; Hu, W. *Chem. Mater.* **2021**, DOI: 10.1021/acs.chemmater.1c02390.
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Metal Halide Perovskite/Organic Semiconductor-based Field-Effect Transistors

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Abstract

Recently, metal halide perovskite, emerging as the next generation semiconducting materials, have gained intense attention due to their remarkable optoelectronic performances of outstanding light absorption, tailored band gap, long charge-carrier diffusion length, as well as narrow emission width. These admirable characteristics of perovskite materials, combined with facile synthesis, good solution processibility, make them suitable candidates for a great variety of applications, such as laser, solar cells, X-ray detection, light-emitting diode, and so on. However, the perovskite materials are blamed for ion migration, which greatly hindered their application in field-effect transistors (FETs). The ions migration of perovskite will result in gate-field screening effect, which further contributes to relatively low charge mobility. Moreover, metal halide perovskite has the innate disadvantages of poor photo/thermal stability, as well as unsatisfactory moisture resistance. To address these issues, we aim to construct perovskite/organic semiconductor (polymer and organic molecule) based FETs. Organic semiconductor can be used to improve stability and charge mobility of perovskite. Benefiting from strong light absorption of perovskite and high charge mobility of organic semiconductors, perovskite/organic semiconductor-based FETs might find their promising applications for neuromorphic computing, photodetectors, non-volatile memory and so on.

Publication List

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Negative phototransistors with ultrahigh sensitivity and weak-light detection based on 1D/2D molecular crystal heterojunctions

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Abstract

Anomalous negative phototransistors (NPTs) that the channel current decreases under light illumination hold potential to generate novel and multifunctional optoelectronic applications. Although a variety of design criteria have been developed to construct such devices, NPTs still suffer from far lower device performance compared to well-developed positive phototransistors. Here, a novel 1D/2D molecular crystal p-n heterojunction, in which p-type 1D molecular crystal (1DMC) arrays are embedded into n type 2D molecular crystals (2DMCs), is developed to produce ultrasensitive NPTs. P-type 1DMC arrays act as a light-absorbing layer to generate photogenerated electron-hole pairs under light illumination, which effectively induce p-doping of n-type 2DMCs through charge transfer, resulting in ineffective gate control and significant negative photoresponses. Impressively, high photoresponsivity (1.9×10^{8}), responsivity (4.3×10^{3} A W-1) and detectivity (1.7×10^{17} Jones) are achieved, which is the highest value in NPTs and one of the highest values among all organic phototransistors. Moreover, the device exhibits intriguing characteristics undiscovered in conventional positive phototransistors, including precise control of the threshold voltage by programming light signals and ultrasensitive detection of weak light. These findings represent a milestone for negative phototransistors, and pave the way for development of future novel optoelectronic applications.

Publication List

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Synthesis of belt-shaped fully fused carbon nanostructures

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Abstract

The synthesis of carbon nanobelts has been an on-going hot spot in organic chemistry owing to their esthetically appealing structures as well as their potential applications in the bottom-up synthesis of single-walled carbon nanotubes. However, their synthesis remains the top challenge and a bottleneck limiting their further applications in the science of carbon nanotubes, which results from the limited synthetic strategies and rare successful examples. Therefore, novel successful examples and new synthetic methods are in need. To overcome the synthetic challenge, we are planning to synthesize a family of novel carbon nanobelts to enrich the system of carbon nanobelts and provide a facile synthetic strategy for their synthesis. This project would not only provide new insights in shrewd design and efficient synthesis of novel aromatic belts but also shed light on understanding the concepts of strain, conjugation, and aromaticity, which are critical for the synthesis of single-walled carbon nanotubes and studying their fascinating properties.

As for topologically unique nanostructures, current studies are limited on the construction of topologically unique macrocycles. There is no previous experience in the synthesis of topologically unique belt-shaped fully fused nanostructures. To develop a synthetic approach and provide successful examples of topologically unique belt-shaped fully fused nanostructures, we are going to employ helicene units to form a helical belt and a MÖbius belt. This study would throw light on rational design and efficient synthesis of topologically unique belts. Besides, these chiral belts may exhibit unexpected properties, such as unique optical properties and fascinating magnetic properties.

Publication List

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The Aromaticity of expanded radialenes and its charged species

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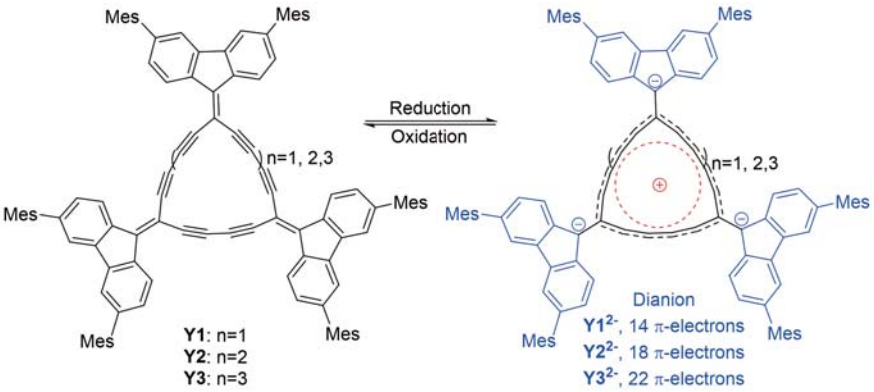
Abstract

A series of aromatic negative charged extended radialenes ($Y1^{2-}$, $Y2^{2-}$ and $Y3^{2-}$) were obtained by in situ chemical reduction of fluorenyl-substituted extended radialene trimer Y1, tetramer Y2 and pentamer Y3. These charged species were proved stable in glovebox and their stability could be attributed to the push-pull effect between fluorenyl units and extended radialene core, which resulted in a positive charged macrocyclic core and corresponding fluorenyl anions. Meantime, the aromatic character of the extended radialene core served as a major driving force of this charge separation. Aromatic character of $Y1^{2-}$ and $Y2^{2-}$ were verified by (VT) NMR spectrometry. $Y1^{2-}$ was observed with a close-shell ground state whereas $Y2^{2-}$ and $Y3^{2-}$ demonstrated open-shell diradical characters. However, the NMR spectra of $Y3^{2-}$ was broad even through cooling down to 188 K due to its large diradical character. The aromaticity of $Y1^{2-}$, $Y2^{2-}$ and $Y3^{2-}$ were further supported by ACID, 2D-NICS, and 3D-ICSS calculations.



Publication List

None

Property Study of Polyradicaloids Systems

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Abstract

Singlet diradicaloids compound and polyradicaloids compound are found to exhibit small singlet-triplet gap and nonlinear optical responses. The unique physical properties open the opportunities for them to become new materials such as organic light-emitting diodes, organic field-effect transistors and Nonlinear optics. Most of the recent research on polyradicaloids is focused on the synthesis of stable radical compounds. It should be noticed that the study of fundamental concepts such as aromaticity and valence tautomerisation of the polyradicaloids systems will also be useful, as those concepts will help researchers to get a better understanding of the electronic interaction in the system and to get more ideas to tune the properties of the polyradicaloids compound.

In our first project, the macrocycle based on Indeno[2,1-b]fluorene was designed. It is assumed that the two structural isomers of the designed macrocyclic compound may exist simultaneously. The valence tautomerisation between two resonance structures 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 are investigated by UV-Vis-NIR spectroscopy and cyclic voltammetry. Theoretical calculations are performed to illustrate the aromatic characteristics of the compounds.

In the meantime, to further understand the aromaticity of polyradicaloids system, macrocycles based on zethrene was synthesized. It is assumed that different sized oligomers may exhibit different aromaticity due to the difference of π electrons. The aromaticity of our ideal products will be characterized by NMR, CV, UV-Vis-NIR spectroscopy and single crystal XRD.

Publication List

None

Two-Dimensional Ferroelectric Dion-Jacobson Perovskite

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Abstract

Two-dimensional (2D) organic inorganic hybrid perovskites (OIHPs) attract numerous attentions for their high environmental stability owing to the inherent hydrophobic interlayer organic cations. <100>-oriented 2D OIHPs play the dominated role in current research and mainly consist of Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) phase. Due to the tight hydrogen bond interaction between perovskite slabs, DJ phase 2D OIHPs present much stronger resistance to harsh atmosphere than their RP counterparts, in which the interaction between perovskite slabs is weak van der Waals interaction. Moreover, the tight interlayer interaction in DJ phase enables weak perovskite-perovskite interaction thus endowing DJ phase 2D OIHPs great potential in highly stable photoelectronic devices. Furthermore, 2D OIHPs are regarded as promising platforms to discover the ferroelectrics because the order and disorder alignment of interlayer organic cations can indue the ferro-paraelectric transition of 2D OHIPs, which expands the application of 2D OIHPs in spintronic and memory devices. Here, we report a ferroelectric 2D DJ perovskite (4AMP)PbBr4 (4AMP= 4-(aminomethyl)piperidinium) possessing the ferroelectricity induced by the order alignment of 4AMP cations. The ferroelectric behaviors are proofed by macro polarization electric field (P-E) test and piezoelectric force microscopy (PFM).

Publication

None

Design and Synthesis of Two-Dimensional Ferroic Hybrid Perovskites

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Abstract

Organic-inorganic hybrid perovskites have elicited tremendous attention in the arena of optoelectronic devices owing to their intriguing physicochemical properties, including large carrier mobility, high photoluminescence efficiency and intrinsic ferroic nature. Among these appealing properties, ferroics, i.e. the general term of ferromagnetism, ferroelectrics, and ferroelastics, denoting some physical characteristics that can be switched by applying external fields, is attracting more interdisciplinary interest as such properties can endow perovskites with unique spontaneous memory characteristics that can be used as non-volatile storage devices, demonstrating promising commercial prospects. However, on account of the multifariousness of organic ligands and complexity of organic-metal interaction, an instructional strategy to design ferroic hybrid perovskites is still lacking. More importantly, whether the coupling of some ferroic features existing in hybrid perovskites, e.g. magnetoelectricity and magnetoelasticity, is disputable and needs to be further explored.

Hence, in this report, we propose an instructive design philosophy and synthetic strategy to prepare two-dimensional (2D) ferroic hybrid perovskites and successfully obtained high-crystalline ferroelectric (3/4-Trifluoromethylbenzylamine)$_2$PbCl$_4$, ferroelastic (S)-(methylbutylamine)$_2$(methylamine)$_{n-1}$Pb$_n$I$_{3n+1}$ perovskites, antiferromagnetic (trifluoromethylbenzylamine)$_2$MnCl$_4$ and ferromagnetic (R/S)-(methylphenethylamine)$_2$CuCl$_4$ perovskites. Their further physicochemical properties are also elaborately investigated. For instance, we observe a long spin-spin relaxation lifetime of ~ 2.81 ns in (trifluoromethylbenzylamine)$_2$MnCl$_4$ perovskite, which is the longest lifetime reported at room temperature. We also demonstrate a first magnetoelectric coupling investigation in chiral (R/S)-(methylphenethylamine)$_2$CuCl$_4$ perovskites, which exhibit a giant magnetocapacitance of ~ 30 %. This work gives an insight into the ferroics and magnetoelectric coupling in 2D hybrid perovskites, paving the pathway for further memory storage and spintronic investigation.

Publication List

None.

Stabilization of 3D $K_{0.2}Na_{1.3}Mn_{0.5}O_2$ via K doping for high efficiency oxygen redox

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Abstract

Even though layered intercalation oxides (classified as two-dimensional oxides) with both cationic and anionic redox chemistry can deliver high discharge specific capacity, they usually face challenges when it comes to long-term stability because oxygen redox reactions always induce gradual yet irreversible structural changes. their poor oxygen redox efficiencies are limited by crystal stability. Herein, we develop propose a doping strategy to tackle this long-standing issue of instability and hence increase the anionic oxidation/reduction efficiency. K-doping is adopted to K is doped to tune two-dimensional (2D) Na1.3Mn0.7O2 (NMO) to three-dimensional (3D) K0.2Na1.3Mn0.5O2 (KNMO), thereby stabilizing the its crystal structure and suppressing irreversible phase transition upon cycling. Besides, KNMO features manganese and oxygen reactive sites. Therefore, with both manganese and oxygen as reactive sites, KNMO delivers higher discharge capacity of (190 mA h g-1) at 5 mA g-1 in the voltage range of 2.0-4.5 V than that of NMO (71.4 mAh g-1) and displays a improved capacity retention after 50 cycles at 50 mA g-1 (83.5 %) compared with that of NMO (< 5 cycles). Our results demonstrate evidence that fabricating intercalation oxides with tridimensional 3D structures are is promising in developing high-efficiency oxygen redox chemistry in for sodium ion batteries.

Publication List

None

Covalent Organic Frameworks for photo- and enzyme tandem catalysis

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Abstract

One-pot multi-step reactions are quite charming, due to their high efficiency as well as simplified flow path. However, combining reaction steps with different mechanism are quite challenging. Except the incompatible reaction conditions of reactions with unmatched mechanism, the lack of catalysts with multiple catalytic sites also contribute to the difficulty of tandem reactions. Benefit from their unique crystalline and porous structure, Covalent organic frameworks (COFs) provide an emerging molecular platform for loading various catalytic sites and thereby designing tandem catalysts. Here, this work designs a series of COFs that have potential to combine photocatalytic sites and enzymes to work synergistically for photo- and enzyme tandem reactions.

Publication List

None

Synthesis and Function of Covalent Organic Framework Crystallites

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Abstract

Covalent organic frameworks (COFs) are a novel class of crystalline porous materials with periodically ordered structures, which exhibit potential applications in various areas such as energy storage, gas adsorption, catalysis and so on. Despite the great progress over the past 16 years, most COFs are produced as polycrystalline powders with small crystalline domains. This situation greatly restricts the complete structure characterization by single-crystal X-Ray Diffraction (SXRD) to precisely determine the atomic positions of COFs. Moreover, lacking single crystal also limits the understanding the uniqueness and nature of this material. Therefore, preparation of COF single crystals is a highly desired yet challenging subject

We are interested in developing the method to grow large single-crystalline two-dimensional (2D) COF and explore their applications in semiconduction. In this project, we focus on the growth of imine-linked 2D COFs single crystals. In this meeting, we will report the literature review, backgrounds and progress of experimental results.

Publication List

None

Design and Functions of Conductive Covalent Organic Frameworks

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Abstract

Tetrathiafulvalene (TTF), known as organic metal, and its derivates are a class of electron-rich molecules with excellent conductive properties. In recent years, superconductive materials based on TTF derivates have become a hotspot. Due to their unique radical status, symmetry, and broad range of corresponding acceptors, TTF derivates are regarded as good candidates for covalent organic frameworks (COFs) systems. COFs are a class of crystalline porous polymer, obtained through dynamic covalent chemistry, which have been explored for light-emitting and semiconducting applications. The latticed structure with predesigned molecular orderings of 2-dimensional COFs provides a possibility for integrating organic metals into the skeleton to prepare conductive materials. In this project, we will synthesize a series of TTF-based COFs with different topologies and construct donor-acceptor systems with various counterions, aiming to establish a library of conductive TTF-based COFs. Then the conductivity and charge behavior of those TTF-based COFs will be investigated. In this workshop, we will report the literature reviews, research background, and progress in experiments.

Publication List

None

Study on Stimulus-responsive Room-temperature Phosphorescent Materials

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Abstract

Room temperature phosphorescent (RTP) compounds which can response to the external stimuli have attracted much attention because they can make full use of excited state energy and have long luminescence lifetime. Most of these external stimuli will lead to some dynamic processes, such as changes in the molecular structure, conformation and distance between molecules, which result in the change of corresponding photo-physical properties. Moreover, compared to host-guest doping system, single-component RTP materials are easier to study the internal mechanism, and have more potential in practical applications. Among these RTP materials, phenothiazine derivatives have attracted much attention due to their unique optoelectronic properties, which mainly include two aspects: 1. Among them, N and S heteroatoms are prone to n-π* transitions due to the existence of lone pairs of electrons, thereby achieving singlet to triplet state 2. Its non-planar butterfly-like configuration can effectively inhibit the π-π accumulation between molecules and reduce the energy lost by the non-radiative transition. Here, a series of phenothiazine derivatives are designed, which aims to realize the stimulus-responsive photo-physical properties in the single-component system.

Publication List

None.

Stable luminescent radicals applied in optoelectronic applications with doublet emission

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Abstract

The doublet emission of radical emitters has shown great potential in organic light-emitting diodes (OLEDs), as it avoids the formation of triplet excitons which limit the electroluminescence efficiency of general emitters. Stable radicals, such as perchlorotriphenylmethyl, tris(2,4,6-trichlorophrnyl)methyl and biphenylmethyl radicals, have been reported showing great stability and luminescent properties. However, discoveries mainly limit on the TTM, PTM and BTM radicals due to their high stability. And the emission wavelength mainly focuses on the deep-red and near-infrared region due to the natural narrow band gap.

Here we explore a new series of stable luminescent radicals, 9-(2,4,6-trichlorophenyl)-9-thioxanthene (TCP-T), 10-methyl-9-(2,4,6-trichloro-phenyl)-10-hydroacridine (TCP-MHA) and 9-(2,4,6-trichlorophenyl)-xanthene (TCP-X), and we also introduce different electron-donating groups to adjust luminescence properties. The role of trichlorophenyl moiety is providing steric hindrance and electron-accepting effect to improve the stability and luminescent performance. These donor-acceptor radicals are expected to have relatively high photostability and blue-shifted emission because of the larger energy gap.

Publication List

None

Design and synthesis of AIE organic functional materials with chemiluminescence for biological applications

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Abstract

Chemiluminescence materials are popularly developed as a kind of novel tools for biological applications in vivo, due to its high penetration depth and avoided background autofluorescence. The widely studied chemiluminescence platforms include luminol, cypridina luciferin analogs, peroxyoxalates, and 1, 2-dioxetanes. In contrast, the chemiluminescence platforms based on 1, 2-dioxetanes are independent of oxidative species and can be triggered by a lot of analytes of interest, which prompts infinite possibilities for the detection of analytes range. Moreover, the easier synthetic routes of 1, 2-dioxetanes, NIR chemiluminescence probes, especially NIR-II, and novel platforms are still the issues to be addressed in the future. In this project, we are interested in developing chemiluminescence probes based on 1, 2-dioxeanes with the aggregation-induced emission property through the energy transfer process and more novel synergistic strategies of chemiluminescence probes for bioimaging and therapy. In this meeting, we will report the literature review, backgrounds and progress of experimental studies.

Publication List

None

Convergent synthesis of oligothiophene-based quinoidal compounds and their properties

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Abstract

Organic semiconductor materials have received extensive research attention in the past decades because of their superior portability, flexibility, and large-area processability. Most organic semiconductor materials have aromatic structures with planar cyclic units that obey the Hückel rule (4n+2 no. of π electrons). In contrast, quinoidal structure breaks the aromaticity of the rings, and the adjacent units are connected by double bonds with smaller bond length alternation. This special electronic structure results unique optoelectronic and magnetic properties. Herein, we synthesized a series of oligothiophene-based quinoids which may exhibit excellent performance as OFET devices. Traditionally, a core unit is prepared, followed by terminal units capped at both ends. In our strategy, we first construct aromatic units as the functionalized terminal groups, then constructing the quinoidal precursor via Stille coupling. This new method allows easy access to quinoidal compounds with variable termini and cores while also improving reaction efficiency. Lastly, we will be testing their performance as OFET devices and study the effectiveness of different termini and core units.

Publication List

None

Synthesis and characterization of conjugated materials based on isoindigo derivatives

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Abstract

Over the past decade, organic semiconductor, especially the near-infrared materials, has made a breakthrough in the fields of optoelectronics, communications, sensing, medical treatment, and imaging. Isoindigo has become a widely used electron-deficient subunit in the donor-acceptor type semiconductor. After a fully manipulation of the original isoindigo unit in semiconductors, researchers turned to do some modifications on the isoindigo unit to further enhance its features like core expanded, halogenated, heterocycle-substituted and peripherally expanded. In this research, we choose the core expanded strategy which means additional conjugated units are inserted into the exocyclic double bond at the core of the isoindigo molecule.

The core expanded structure was first reported by Kelly’s group. Although it can be applied into the photovoltaic devices alongside some common donors and acceptors, due to its alky chain number, the performance was not so good. We intend to replace the N atom into O and S atom. There is one question needs to be discussed that the choice of the alkyl chain will strongly influence the application, because the substitution number decreased, the solubility will be affected. By inducing some heteroatom to lower the LUMO level of the bisisoindigo unit to better improve its performance as an electron acceptor, we think it will red-shifted more when applied into the DA type materials.

Publication List

None

Thiophene-based Ladder-type molecules for High-performance Conjugated Organic Semiconductors

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Abstract

The study of organic semiconductors is a field with great scientific significance and broad application prospects. Organic semiconductors overcome the inherent shortcomings of inorganic semiconductors such as high cost, high energy consumption and fragility, and also endows materials with new characteristics such as light weight and flexibility. Ladder molecules are unique to construct organic semiconductor materials, because their main chain is composed of fused rings. The limitation of bond rotation greatly prevents the rotation of conjugate skeleton, bringing interesting properties and potential applicability as functional organic materials. For example, Indacenodithiophene (IDT) has been widely used as the central core to design high-performance acceptor-donor-acceptor (A-D-A)-type non-fullerene acceptors (NFAs). The energy level, band gap, molecular stacking distance, and charge transport of the target material can be directly affected by the number of fused rings, heteroatoms, spatial configuration and side chain steric hindrance. Considering the synthesis of ladder molecules with alkyl-substituted side chains is a powerful strategy to improve device performance, we are trying to provide effective methods for the design and synthesis of novel and high-performance thiophene-based ladder structures.

Publication List

None

Fluorescent Lateral-Flow Immunoassays for Thrombus-marker Detection

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Abstract

Thrombosis is a hidden killer, difficult to detect and often sudden, resulting in high morbidity and mortality, and is a life-threatening disease across the globe. Consequently, developing rapid, cheap, and sensitive methods for the determination of biomarkers is of paramount importance in medicine, point of care (POC) technology has been playing a key role in clinical practice. In particular, Lateral-flow assays (LFAs) are quick, simple, and cheap assays to analyze various samples at the POC field. D-dimer is a soluble fibrin degradation product that results from the ordered breakdown of thrombi by the fibrinolytic system, which is commonly served as a valuable marker of diagnosis of venous thromboembolism (VTE). In this work, we design and fabrication of D-Dimer detected nanoparticle-based lateral-flow immunoassays and employed the principle of immunochromatography in the “sandwich” format. We demonstrate that the density of D-Dimer antigens can be quantified and measured with an enhanced sensitivity using this simple laser optical analysis.

Publication List

None

Imide-based electron transport materials for perovskite solar cell

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Abstract

Perovskite solar cell (PSC) as the third-generation emerging photovoltaics has achieved considerable progress with certificated power conversion efficiency surpassing 25%. Considering the strengths of solution processability, mechanical flexibility and versatility of chemical structures and properties of the active layer, PSC holds highly potential for alternating the silicon-based solar cells. However, there are still many challenges existing for research and industry as exhibiting limited stability, moderate efficiencies and higher cost. Although inorganic electron transport materials including TiO_2, SnO_2, ZnO have been extensively studied in PSC as electron transport layer, high photocatalytic activity induced perovskite degradation, high temperature annealing, and surface defects induced unsatisfied performance put great barriers in the commercialization of PSC technology. Organic electron transport materials that possess lower processing cost and straightforward synthetic protocols, higher solubility, and tunable optoelectronic properties through suitable molecular engineering are deemed as new solution for overcoming above drawbacks of metal oxide. Here, based on classic n-type organic semiconductor electron deficient construction moiety, we designed imide-based small molecular electron transport materials which could self-assemble on metal oxide surface due to the combination of carboxylic acid or phosphonic acid. The solely self-assembled electron transport layer could attain a power conversion efficiency of 16.4%.

Publication List

None

Polymeric Field-effect Transistors Achieved by Solution Methods and Understanding of Morphology-Performance Relationships

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Abstract

Producing polymeric Field-effect transistors with low-cost and scalable solution fabrication methods in an ambient environment could be considered as an attractive route for large-scale production of organic filed-effect transistors (OFETs) to achieve numerous applications.

Solution shearing is a technique that applies the shearing force caused by the single-axis movement between the substrate and the shearing blade to guide the coating solution. During the guiding process, the shearing force produced by the relative movement will induce the solution to form a meniscus shape. The solution evaporates on the meniscus and has the highest evaporation rate at the tip of the meniscus. Such enhancement of evaporation at the tip could modulate the nucleation and deposition of molecules to form a uniformly arranged film.

It is well known that the interface morphology of conjugated polymers thin film plays a dominant role in determining carrier transportation property which is crucial to achieving high mobility. The morphology is highly dependent on the film processing methods but the film formation mechanism for solution methods is still not clear.

Charge modulation spectroscopy (CMS) could provide a novel perspective to reveal the carrier transportation mechanism in different organic dielectric interface morphology. CMS is an electro-optical spectroscopic method that measures the charge-induced optical transmission variation by probing the accumulated charge at the interface directly. It shows an advantage over the conventional characterization methods in probing the accumulation and transportation behavior of charge carriers in OFETs.

Publication List

None

The Synthesis of Graphyne Wheel

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Abstract

Graphyne is a low energy phase of carbon consisting of flat sheets with only sp and sp^2 carbons. It has been predicted to be a moderate bandgap semiconductor (Eg = 1.2 eV) with interesting non-linear optical property. However, direct synthesis of graphyne is of great challenge. Dehydrobenzoannulenes (DBAs), as the model structures of graphyne, has attracted increasing research attention. Investigation of DBAs can help to establish a better understanding of the properties of graphyne. However, only some simple DBAs have been synthesized. Larger and more complex DBAs are rarely reported due to great synthetic challenges. Graphyne wheel is one of the most important models. The highly symmetric structure and intrinsic electronic properties have prompted scientists to seek for possible synthesis of graphyne wheel, but there is no successful method reported so far. Here, our strategy for the synthesis of graphyne wheel will be introduced, which involves a 12-fold stille coupling as the key step. It is a promising method to prepare graphyne wheel.

Publication List

None

Solution-processed Nanographenes for NIR Laser Materials

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Abstract

Nanographenes have been demonstrated to be outstanding materials for optical devises due to their tunable energy gaps and optical properties. Taking the advantages of aromatic stability and molecular symmetry, a myriad of structures with electronic transitions that span the UV-Vis and near IR regions can be prepared. More importantly, nanographene molecules can be designed and tailored for precise optical application such as laser materials and luminance materials that emit light at specific wavelengths. However, synthesis of nanographenes with good efficiency has long been a major obstacle. Besides, it is also crucial to investigate and establish a correlation between the chemical structures of nanopgraphene including molecular size and edge structure and their optical properties in order to design and prepare nanographene with better laser performance. In my study, a bottom-up approach was employed for the synthesis of a new-type nanographene with both zigzag and armchair edges. Firstly, we applied a radical-radical coupling reaction as a key step for the synthesis. This type of reaction has rarely been explored for the synthesis of nanographenes. In our result, this reaction has demonstrated high efficiency for the preparation of nanographene. Additionally, there is currently lack of study to investigate how the presence of both edge structure can impact their performance as laser devices. The nanographenes prepared may help to fill up this knowledge gap. The nanographenes were well characterized with X-ray crystallography, NMR, and UV-VIS spectra assisted with computational calculations.

Publication List

None

Zethrene-based diradicaloids

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Abstract

Zethrene can be regarded as a Z-shaped polycyclic aromatic hydrocarbon molecule composed of two phenalenyl units. Zethrene with extension along y axis attains higher order giving heptazethene, octazethrene; zethrene with extension along x axis can grow into dibenzozethrene, superzethrene species, and other extended zethrenes. These zethrene derivatives exhibit unusual open-shell diradical characters and unique magnetic properties, which can be verified by VT-NMR, ESR, and DFT calculations. Our initial aim was to synthesize a laterally extended zethrene derivative called superzethrene; however, an unexpected brominated dibenzozethrene derivative was obtained. X-ray crystallographic analysis revealed its structure, and VT-NMR spectroscopy and DFT calculations were applied to study its open-shell diradical character. Meanwhile, nickel-catalyzed transannular cyclization was found efficient to provide dibenzozethrene. Based on this method, a novel zethrene-based diradicaloid with polyradical characters was designed, where a series of synthetic approaches and stabilization strategies were explored owing to its intrinsic instability. Bulky mesityl groups were incorporated into the reactive sites so as to kinetically stabilize the structure, whereas peripheral n-butyl chains helped boost the solubility.

Publication List

None

Workshop Schedule

Center 2: Organic Chemistry			
Symposium Chair: Lin Zhikeng			
Morning Session			
	Presenter	**Title**	**Supervisor**
Session Chair: Lin Zhikeng			
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	Direct Construction of BINAM Derivatives *via* Ni-catalyzed Reductive Homocoupling	Lu Yixin
9:40-10:00	Zhu Kun	Regiodivergent Sulfonylarylation of 1,3-Enynes *via* Nickel/ Photoredox Dual Catalysis	Lu Yixin
10:00-10:20	Lin Zhikeng	Rhodium-catalysed Enantioconvergent Isomerisation of Remote Alkenyl Amines	Zhao Yu
10:20-10:40	Gao Yaru	Access to Diverse *N*-heterocycles through Borrowing Hydrogen	Zhao Yu
10:40-11:00: Break			
Session Chair: Lin Zhikeng			
11:00-11:20	Pan Jiaoting	Pd-catalyzed [4+4] Cycloaddition of Azadienes with Simple 1,3-Dienes to Construct Eight-membered Heterocycles	Zhao Yu
11:20-11:40	Dong Xiaohan	*N*-Hydroxyphthalimide Esters Involved Phosphine-catalyzed Asymmetric [3+2] Annulation and Subsequent Decarboxylation Reactions	Ma Jun'an & Lu Yixin
11:40-12:00	Yuan Ye	Photo-induced sp^2 C-F Bond Olefination of Multifluorinated Arenes	Ma Jun'an & Wu Jie
12:00-12:20	Zhao Taoqian	Access to Enantioenriched γ,σ-Unsaturated Amido Esters *via* Cobalt/Photoredox Dual Catalysis	Ma Jun'an & Ge Shaozhong
Lunch Break			
Afternoon Session			
	Presenter	**Title**	**Supervisor**
Session Chair: Luo Xiaohua			
14:00-14:20	Huang Qingqin	Asymmetric NiH-catalyzed Hydroalkylation of Alkenes	Lu Yixin
14:20-14:40	Guo Jiami	Phosphine-catalyzed Photochemical Strategies for Stereoselective Interception of Hydroxy-o-quinodimethanes	Lu Yixin
14:40-15:00	Sun Yuli	Synthesis of Axially Chiral Compounds	Lu Yixin
15:00-15:20	Zou Gongfeng	Divergent Access to Ten to Thirteen-Membered Heterocycles Containing *Z*/*E*-Controllable Trisubstituted Alkenes through Pd-catalyzed cycloaddition	Zhao Yu

15:20-15:40	Diao Huanlin	Stereoselective Synthesis of Piperidine *via* Iridium-catalyzed Borrowing Hydrogen Strategy	Zhao Yu
15:40-16:00: Break			
Session Chair: Luo Xiaohua			
16:00-16:20	Liu Yufeng	Borrowing Hydrogen Reaction between Allylic Alcohol and Amine	Zhao Yu
16:20-16:40	Zhang Zhiqi	Photo-induced Hydrodifluoromethylation of Unactivated Olefins with $ClCF_2H$	Ma Jun'an & Wu Jie
16:40-17:00	Zhai Yixuan	Cobalt-catalyzed Asymmetric Hydroboration/Cyclization of Trifluoromethylated 1,6-Enynes	Ma Jun'an & Ge Shaozhong
17:00-17:20	Luo Xiaohua	Catalytic Regioselective Hydrocarbofunctionalization of Alkenes by Sequential Carbonickelation-Hydride Transfer	Ma Jun'an & Koh Ming Joo

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-disubstituted carbazolones have been established. Different substituted carbazolones could be employed in this process, which is catalyzed by a chiral phosphine derived from an amino acid, affording 3,3-disubstituted carbazolones in good yield and excellent enantioselectivity. This methodology will be applied in total synthesis of *Aspidosperma* alkaloid. The key synthetic features include a reductive-amination cyclization and nucleophilic substitution cyclization to install its key carbocyclic skeleton. This strategy will be applicable for assembling divergent *Aspidosperma* alkaloids possessing this key skeleton.

Publication List

Chen, Y.; Wang, J.; Lu, Y. Decarboxylative 1,4-carbocyanation of 1,3-enynes to access tetra-substituted allenes via copper/photoredox dual catalysis. *Chem. Sci*. **2021**, *12*, 11316.

Direct Construction of BINAM Derivatives via Ni-catalyzed Reductive Homocoupling

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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 such as BINOL, BINAP, BINAM and NOBIN. Axial chirality is also a key feature of many natural products and most of them exhibit outstanding biological activities including vancomycin, streptonigrin and michellamines. Among these, the design of synthetical protocols towards BINAM derivatives is an attractive topic, owing to their broad range of applications in an array of fields including auxiliary ligands, catalysis, and molecular imaging. However, although [3,3]-rearrangement and enantioselective aryl-aryl cross coupling pathway were developed to access BINAM derivatives, the main strategies are still relying on dynamic kinetic resolution. Therefore, a direct and general synthetic strategy to access BINAM derivatives would greatly advance the preparation of BINAM ligands.

Publication List

None

Regiodivergent Sulfonylarylation of 1,3-Enynes via Nickel/Photoredox Dual 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

Chen, Y.; Zhu, K.; Huang, Q.; Lu, Y. ***Chem. Sci.***, 2021, **12**, 13564-13571.

Rhodium-catalysed Enantioconvergent Isomerisation of Remote Alkenyl 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 in a reaction cascade to access amines with two stereogenic centres with high enantioselectivity and diastereoselectivity.

Publication List

None

Access to Diverse *N*-heterocycles through Borrowing Hydrogen

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Abstract

Nitrogen-containing heterocycles represent an important role in pharmaceutical and agrochemical industries, for which many asymmetric synthetic methods have been developed. Amination of alcohols through the borrowing hydrogen, as one kind of green chemistry, has attracted much attention due to its overall redox-neutral nature and minimal waste generation. Our group has a continuous interest in chiral *N*-heterocycles synthesis through borrowing hydrogen. Chiral benzomorpholine derivatives are one type of important and unique building blocks in developing biologically active molecules, and both C2- or C3-substituted benzomorpholine derivatives have important applications. However, the developed methods to access chiral benzomorpholines require well designated substrates or harsh reaction conditions. In addition, asymmetric synthesis of benzomorpholine with different substitution patterns need substrates with different structural backbones. In this project, we developed three types of enantioselective borrowing hydrogen reactions to synthesize diverse *N*-heterocycles, including intramolecular asymmetric dynamic kinetic amination of amino alcohols, asymmetric intramolecular amination of amino alcohols and synthesize seven-membered *N*-heterocycles. Notably, substrates of these reactions were converted from the same key pro-substrate through the Smiles rearrangement, resulting in various C2- or C3-substituted benzomorpholine derivatives with high conversion and enantioselectivity under relatively mild reaction conditions.

Publication List

None

Pd-catalyzed [4+4] Cycloaddition of Azadienes with Simple 1,3-Dienes to Construct Eight-membered Heterocycles

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Abstract

We report herein the first enantioselective [4+4] cycloaddition of azadienes and simple 1,3-dienes to form eight-membered heterocycles in high efficiency and enantioselectivity via palladium catalysis. Easily accessible simple 1,3-dienes and the nature of cycloaddition provide this reaction with high atom economy and synthetic value. In mechanism, palladium complex serves as a π- Lewis base catalyst to activate 1,3-dienes, which makes it possible to achieve α,δ-difunctionalization of simple 1,3-dienes.

Publication List

1. Yang, G.; Pan, J.; Ke, Y.-M.; Liu, Y.;* Zhao, Y.* *Angew. Chem. Int. Ed.* **2021**, *60*, 20689.
2. Jiang, Y.; Pan, J.; Yang, T.; Lim, J. J. H.; Zhao, Y.*; Koh, M. J.* *Chem* **2021**, *7*, 993.

N-Hydroxyphthalimide Esters Involved Phosphine-catalyzed Asymmetric [3+2] Annulation and Subsequent Decarboxylation Reactions

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Abstract

Phosphine-catalyzed asymmetric annulation reactions have shown remarkable progress and emerged as a powerful tool to construct functionalized desired cyclic structures that have important applications in physiological and biological areas. Among them, [3+2] cycloaddition of alkenes with allenoates is one of the most classical reaction modes and has many valuable works reported. However, this methodology is limited by its substrate design, which requires alkenes contain at least one electron-withdrawing group. Considering NHP esters involved decarboxylations are useful strategy to construct new C-C or C-X bonds, introducing NHP ester group into alkene design might provide the traditional phosphine-catalyzed annulation with more flexibility in applications. Herein, I mainly introduce phosphine-catalyzed [3+2] annulation employing the MBH adducts and intramolecular allene-olefin [3+2] cycloaddition. Highly enantioselective five-member ring products could be 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 sp^2 C-F Bond Olefination of Multifluorinated Arenes

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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 functionalization must be developed. For the photo-induced C-F olefination of multifluorinated arenes, only one work has been reported, and this method needs the aliphatic alkynes as substrates and all the products are internal alkenes. So it is necessary to develop a method to get the C-F olefination that could tolerate aryl-substituted alkenes and give the terminal alkenes product. Herein, we propose an efficient strategy for branchselective, formal alkene–multifuorinated arene cross-coupling via sulfinate-assisted photoredox catalysis. This versatile protocol utilizes a sequential radical addition, radical coupling, and β-elimination protocol, allowing for the construction of branched aryl-substituted terminal alkenes from simple starting materials under mild conditions.

Publication List

None

Access to Enantioenriched γ,σ-Unsaturated Amido Esters via Cobalt/Photoredox Dual Catalysis

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Abstract

Enantiomerically pure γ,δ-unsaturated amido acids and their derivatives are versatile intermediates in organic synthesis. They can be readily converted into a variety of useful building blocks in nonproteinogenic amino acids, antibiotics, and other biologically active molecules. However, the cost of enantiomerically pure γ,δ-unsaturated amino acids is too high and greatly limited their applications. Therefore, to develop an efficient method to synthesis of γ,δ-unsaturated amino acids is highly desired. The reductive coupling between internal alkyne and dehydro-amino esters is a more efficient and straightforward method to prepare γ,δ-unsaturated amido esters. And this method has never been reported due to the challenges to overcome the steric effect of di-substituted alkene and to control the enantioselectivity due to the enantio-determining step was asymmetric protonation, which was not under the control of ligand on a metal center. We initially screened the reactivity of this reaction and good yields have been achieved (78%). However, the enantioselectivity was limited to 80% ee. Further studies will be focusing on the optimization of the enantioselectivity of model substrate and the studies of the scope of this reaction.

Publication List

None

Asymmetric NiH-catalyzed Hydroalkylation of Alkenes

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Abstract

Novel carbon–carbon bond construction protocols extend our imagination of creating amazing synthetic methods of sophisticated organic molecules. Although many well-known reactions are efficient for the formation of C(sp^2)–C(sp^3) and C(sp^3)–C(sp^3) bonds, such as Wacker process, olefin metathesis, Heck reaction and so on, direct use of readily available alkenes in a formal fashion of hydrocarbonation is still a popular field waiting to be developed. Recently, Nickel-hydride (NiH) catalysis has emerged as prevalent strategies to build up carbon-carbon bonds, especially C(sp^3)–C(sp^3) bonds, with excellent regioselectivity and stereoselectivity. Our group is specifically interested in rapid construction of complex chiral molecules with center and axial chirality, and it is plausible to utilize Ni-H catalyzed hydroalkylation to build up chiral cyclopropane derivatives and useful axially chiral compounds.

Publication List

None

Phosphine-catalyzed Photochemical Strategies for Stereoselective Interception of Hydroxy-o-quinodimethanes

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Abstract

Photochemistry is currently emerging as a complementary and more sustainable approach in synthetic chemistry. The unprecedented reactivity of excited organic molecules under light irradiation has tremendously expanded the playground for new reaction discovery. Since the discovery of *ortho*-alkyl aromatic ketones to form the corresponding hydroxy-*ortho*-quinodimethane upon excitation by ultraviolet light, some attempts have been made to use a chiral catalyst to enantioselectively trap the photoenol, which only limited in the chiral amine catalysis. The field of asymmetric phosphine catalysis has gained tremendous advancement in the past decades, owing to the introduction of kaleidoscope of chiral phosphine catalysts and the discovery of new modes of activation in phosphine-catalyzed reactions. Our group has developed a series of novel amino acid-derived phosphine catalysts and made substantial progress on annulation process and γ-addition. To enrich the catalytic system for stereoselective trapping of the photoenol, we proposed that phosphine-catalyzed enantioselective interception of Hydroxy-*o*-quinodimethanes via MBH reactions. Herein, we present the first example of phosphine-catalyzed photochemical strategies for stereoselective interception of hydroxy-*o*-quinodimethanes by using the amino acid-derived phosphine catalyst developed by our group. It provides a new reaction pattern for the enantioselective trap of the hydroxy-*o*-quinodimethanes and some insight for the design of diverse mechanisms.

Publication List

None

Synthesis of Axially Chiral Compounds

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Abstract

Chiral substances are widely present in nature, and the axial chirality is a special form of chirality. At present, due to the widely applicability of axial substances, more and more scientists focus on developing new method to synthesize axial compounds. There are four main synthetic methods for the construction of biaryl axis chiral compounds: transition metal-catalyzed cross-coupling of aryl compounds, oxidative coupling methods, chirality transfer methods, de novo aromatic ring construction methods, kinetic resolution methods. Under the background, the example about 3,3-rearrangment to synthesize axil compounds are very rare. Therefore, if we design a reactant which could undergo interrupted Pummer reaction, and through 3,3-rearrangement to get the axially chiral products, it can provide a new method to synthesize axial chiral compounds.

Publication List

None

Divergent Access to Ten to Thirteen-Membered Heterocycles Containing *Z/E*-Controllable Trisubstituted Alkenes through Pd-catalyzed cycloaddition

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Abstract

Medium-sized rings and macrocycles commonly exist in natural products and bioactive molecules. The synthesis of these medium-sized rings and macrocycles, however, still remains a great challenge for catalytic method development. Out of the different synthetic strategies developed for medium-sized ring and macrocycles formation, intramolecular cyclization or ring expansion is most explored. As an alternative and synthetically flexible approach, intermolecular dipolar cycloaddition provides a significant advantage of directly coupling two building blocks (serving as dipoles and dipolarophiles) to produce medium-sized rings and macrocycles. However, success along these lines remains limited, with cycloaddition of only a few classes of 1,4-dipolarophiles reported in the literature. Here we develop a class of novel, adjustable 1, $n_{(n=6\text{-}9)}$-dipoles, and use them in Pd-catalyzed [4+$n_{(n=6\text{-}9)}$] cycloaddition to deliver a series of ten to thirteen membered heterocycles containing *Z*/*E*-controllable trisubstituted alkenes.

Publication List

None

Stereoselective Synthesis of Piperidine via an Iridium Catalyzed Borrowing Hydrogen Strategy

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Abstract

Nitrogen-containing heterocycles are significant structural components in pharmaceutic. In particular, the most prevalent piperidine motif was found in a total of 72 unique small-molecule drugs. Recently, saturated heterocycles bearing sp^3-stereogenic centers have attracted numerous attention for their potential in the exploration of novel, three-dimensional biological and chemical space. However, installing stereogenic center at specific position of the saturated heterocycles from racemic substrates remains a challenging goal. Herein, we present an enantioselective synthesis of piperidine enabled by cooperative catalysis of Iridium catalyst and chiral phosphoric acid with high yield and high enantioselectivity. This reaction employed two sequential borrowing hydrogen processes to achieve overall redox-neutral synthesis without stoichiometric oxidant and demonstrated environmentally benign transformation.

Publication List

None

Borrowing Hydrogen Reaction between Allylic Alcohol and Amine

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Abstract

Chiral amines are widely found in natural products and drugs, and traditional synthetic methods for chiral amines usually produce equivalent pollutants. Although asymmetric hydrogenation method has higher atom economy and less pollution, high-pressure hydrogen is flammable and potentially explosive. In comparison, borrowing hydrogen reaction has many advantages, such as high atom economy, no pollution with only water as side products and no need to use dangerous hydrogen.

There have been many reports on the borrowing hydrogen reaction between alcohols and amines. However, borrowing hydrogen reactions using allylic alcohols and amines are rarely reported. Allylic alcohol usually makes borrowing reaction more complicated, because allylic alcohol will transfer to α, β-unsaturated ketone through dehydrogenation process, and there will be a problem of chemo-selectivity in next step, nucleophilic attack. We tried different combinations of allylic alcohol and amine, and obtained heterocyclic compounds with medium to good yields. Next, we will optimize the enantioselectivity and try to synthesize various types of heterocyclic structures.

Publication List

None

Photo-induced Hydrodifluoromethylation of Unactivated Olefins with $ClCF_2H$

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Abstract

Chlorodifluoromethane ($ClCF_2H$), the major component of Freon, is a bulk industrial raw material used for production of fluorinated polymers. It has great potential to serve as cost-efficient and straightforward feedstock for the synthesis of some important fluorinated compounds. However, due to the high BDE of C-Cl bond (87 kcal/mol), it is difficult to realize its activation and transformation. So far, most of reactions go through the pathway of difluorocarbene intermediate.

Herein, we first reported commercial-available amine-boranes as chloride atom transfer reagents to realize hydrodifluoromethylation of unactivated olefins. Under the radiation of blue light, amine-boryl and difluoromethyl radicals were generated in this reaction. Mono-, di- or trisubstituted olefins, which bear hydroxyl, tosylate, chloro, ester, ketone, amide, cyano groups, were all well tolerated, providing the desired products in excellent yields (up to 99%). In addition, post modification of some drug molecules and natural products were achieved with good yield using this method. Further studies on mechanism of this transformation and to develop some new reactions with this strategy will be the subjects of future work.

Publication List

None

Cobalt-catalyzed Asymmetric Hydroboration/Cyclization of Trifluoromethylated 1,6-Enynes

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Abstract

Heterocyclic five-membered ring with stereogenic center and functional motifs has drawn enormous attention as they present widely in bioactive molecules and natural products. Transition-meta-catalyzed cyclization with simultaneous functionalization of enynes is a direct and useful method to efficiently construct cyclic compounds. Incorporating trifluoromethyl group into organic compounds is a challenging subject but with multiple application as -CF_3 motif exists in vast pharmaceutical compounds and agrochemical products. With consideration of the unique chemical properties and synthetic value, here we present a cobalt catalyzed enantioselective hydroboration/cyclization of trifluoromethylated 1,6-enynes to access chiral five-membered lactones with -CF_3 motif. So far, the reaction can tolerate a wide range of mono- or di-substituted 1,6-enyne with excellent enantioselectivity (90-99% ee) and decent yield. Further studies to reveal the detailed mechanism of this transformation and to develop Co-catalyzed asymmetric functionalization and cyclization of enynes to deliver trifluoromethylated stereo-center will be the future tasks.

Publication List

None

Catalytic Regioselective Hydrocarbofunctionalization of Alkenes by Sequential Carbonickelation-Hydride Transfer

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Department of Chemistry, National University of Singapore, Singapore

Abstract

Alkene hydrocarbofunctionalization is one of the most important classes of chemical transformations. In this field, metal-catalyzed hydroarylation reactions of unactivated aliphatic C=C bonds can deliver valuable products with aryl- and heteroaryl-substituted carbon centers, so that considerable efforts have been devoted to develop this method. To date, a number of reports in intermolecular linear (anti-Markovnikov)-selective transformations using arenes, aryl nucleophiles, or electrophiles have been disclosed. By comparison, the more compelling branched (Markovnikov)-selective variants, which can furnish entities containing tertiary or quaternary stereogenic centers, are scarce.

To achieve this goal, herein, we report that catalytic amounts of a dimeric Ni(I) complex and an exogenous alkoxide base promote Markovnikov-selective hydroarylation (alkenylation) of unactivated and activated olefins using organobromides or triflates derived from widely available phenols and ketones. Contrary to previous dual-catalytic methods that rely on metal-hydride atom transfer (MHAT) to the olefin prior to carbofunctionalization with a cocatalyst, our mechanistic evidence points toward a nonradical reaction pathway that begins with site-selective carbonickelation across the C=C bond followed by hydride transfer using alkoxide as the hydride source. By using this method, products bearing aryl- and alkenyl-substituted tertiary and quaternary centers could be isolated in up to 95% yield and >99:1 regioisomeric ratios.

Publication List

Liu,C.-F.; **Luo, X.**; Wang, H.; Koh, M. J. *J. Am. Chem. Soc.* **2021**, 143, 9498

Workshop Schedule

Center 2: Functional materials				
Symposium Chair: Xie Jianping				
2022/01/08				
		Presenter	**Title**	**Supervisor**
	Session Chair: Zhang bihan			
	9:00-9:20	Zhang Shiyu	Positive-charged and ultrathin nanofiltration membranes for Mg^{2+}/Li^{+} separation	Jiang Zhongyi & Zhang Sui
	9:20-9:40	Pu Yunchuan	Hybrid COF/ZIF-8 nanosheets as seeds for the growth of ultrathin molecular sieving membrane	Jiang Zhongyi & Zhao Dan
	9:40-10:00	Gong Xiaoting	Design and synthesis nanoparticles with AIE feature for transparent	Liu Bin
	10:00-10:20	Cheng Wei	Multimodal Imaging Guided Photothermal Therapy for Targeted Brain Tumor Treatment	Liu Bin
	10:20-10:40	Lin Yingzheng	Revealing the composition-dependent structure evolution fundamentals of bimetallic nanoparticles through the inter-particle alloying reaction	Xie Jianping
	Break 10:40-11:00			
	Session Chair: Lin Yingzheng			
	11:00-11:20	Liu Zhihe	Molecular-Level Insight of Ligand Effect on the Electrophilicity of Au(I) in Au NCs for Electrocatalysis	Xie Jianping
	11:20-11:40	Zhang Bihan	Exquisitely Functionalize the Surface of $Au_{25}(SR)_{18}$ via a Two-Phase Ligand Exchange Method	Xie Jianping
	11:40-12:00	Liu Zhuang	Novel NIR-Emitting Halide Perovskite Single Crystals	Liu Xiaogang
	Session Chair: Zhang bihan			
	14:00-14:20	Gao Xiong	Photoexcitation Induced Phonon Coupled Non-Radiative Energy Dissipation in Organic Charge Transfer Crystals	Liu Xiaogang & Hu Wenping
	14:20-14:40	Zhao He	low-dimensional Halide Perovskites with Organic Functional Molecule Layers for X-ray Detection	Liu Xiaogang
	14:40-15:00	Ma Yuhan	Three-dimensional Carbon as Inorganic Filler toward Self-healing Composite Solid-Sate Electrolyte for All Solid-State Lithium Metal Battery	He Chunnian & Andrew Barnabas Wong
	15:00-15:20	Zhang Hanwen	Application of Molecular Dynamic Simulation in Functional Materials	He Chunnian & Sow Chorng Haur
	15:20-15:40	Yan Zhicheng	MOF-based materials for electrocatalytic applications	He Chunnian & Loh Kian Ping
	Break 15:40-16:00			
	Session Chair: Lin Yingzheng			
	16:00-16:20	Deng Hao	Machine learning aided synthesis of polyamide nanofiltration membrane	Jiang Zhongyi & Zhang Sui

			with high selectivity and permeability	
	16:20-16:40	Lyu Bohui	Anion Transport in Functional Covalent Organic Framework: A Molecular Simulation Study	Jiang Zhongyi & Jiang Jianwen
	16:40-17:00	Shan Huiting	Atomically Precise Robust Gold Nanoclusters as Peroxidase Mimics for tandem Catalysis	Jiang Zhongyi & Xie Jianping
	17:00-17:20	Cao Lei	Selenium-Containing AIEgens for Combined Immunotherapy and Photodynamic Therapy	Liu Bin
	17:20-17:40	Liu Shitai	In-Situ Synthesized Polymer Photosensitizers for Cancer-Cell-Activated	Liu Bin
	17:40-18:00	Wang Tongtong	Organic Emitters for Device and Biological Applications	Liu Bin

Center 2: Functional materials				
Symposium Chair: Xie Jianping				
2022/01/09				
		Presenter	**Title**	**Supervisor**
	Session Chair: Zhang bihan			
	9:00-9:20	Liu Xianglong	Design and Synthesis D-A-D Type Near-infrared II Fluorescent Dye Based on Strong Acceptor for PDT/PTT Cancer Therapy	Liu Bin
	9:20-9:40	Mu Chuan	Composition-dependent catalytic selectivity of Au_xAg_{25-x} alloy nanoclusters for oxygen reduction reaction	Xie Jianping
	9:40-10:00	Lin Hongbin	Synthesis of AIE-Type Luminescent Metal Nanoclusters through Etching Reaction	Xie Jianping
	10:00-10:20	Hou Jie	Chemical Reaction Kinetics of Gold Nanoclusters for High Scale Synthesis	Xie Jianping
	10:20-10:40	Liu Sirui	High order, non-Hermitian, Floquet Topology and knot theory	Liu Xiaogang& Gong Jiangbin
	Break 10:40-11:00			
	Session Chair: Lin Yingzheng			
	11:00-11:20	Jiang Zhengzhi	Nanoscale NMR sensor based on NV centers in diamond	Liu Xiaogang
	11:20-11:40	Qiu Jian	Bulk Photovoltaic Effect in Chiral Perovskite for Self-Powered Circularly Polarized Light	Liu Xiaogang
	11:40-12:00	Sun Guangxin	The Effect of Anion Impurities in Electrolyte for Electrochemical CO_2 Reduction	He Chunnian & Andrew Barnabas Wong
	12:00-12:20	Wang Xin	MOFs modified copper oxide materials for CO_2 electrochemical reduction reaction	He Chunnian & Andrew Barnabas Wong

Hybrid COF/ZIF-8 nanosheets as seeds for the growth of ultrathin molecular sieving membrane

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Abstract

Two dimensional (2D) nanomaterials are intensively studied since the discovery of graphene in 2004. Benefiting from the unique structural features, 2D materials, such as graphene oxide (GO), metal organic framework (MOF), and covalent organic frameworks (COF) nanosheets, are promising for the membrane-based gas separations. In my work, I would like to prepare a composite membrane containing COF nanosheets for C_3H_8/C_3H_6 separation. Highly porous COF nanosheet can be filtrated on the substrate and induces the formation of ultrathin ZIF-8 layer. To be specific, EB-COF/ZIF-8 hybrid nanosheets were adopted as gutter layer and covered by a continuous ZIF-8 layer through second growth. Two selective layer including COF/MOF hybrid structure and continuous ZIF-8 cover possess dual transport way within the membrane, which will enhance the gas separation performance.

Publication List

1. **Pu, Y**.; Yang, Z.; Wee, V.; Wu, Z.; Jiang, Z.; Zhao, D. Amino-Functionalized NUS-8 Nanosheets as Fillers in PIM-1 Mixed Matrix Membranes for CO2 Separations. Journal of Membrane Science 2022, 641, 119912.

Positive-charged and ultrathin nanofiltration membranes for Mg^{2+}/Li^{+} separation

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Abstract

Lithium (Li) resources have aroused considerable attention due to the rapid development of lithium-ion batteries, which serve us in different end-use markets. Salt lake brines account for ≈70% of recoverable Li on earth and the majority of them feature a high Mg^{2+}/Li^{+} ratio (>34). Nanofiltration (NF) membranes bearing the high retention of multivalent salts confer economical means to alleviate global Li scarcity. However, most efforts have been focused on negative-charge NF membranes, exhibiting poor rejection to Mg^{2+}. Herein, we fabricate positive-charge NF membranes through support-free interfacial polymerization of Triaminoguanidine (TG) carrying functional guanidyl group and trimesoyl chloride (TMC). Owing to the weakly pH-dependent and supercharged nature of TG monomer, the optimal membrane exhibits an ultrahigh Mg^{2+} rejection (>98%) from highly concentrated $MgCl_2$ solution and is coupled with long-term superior stability. In addition, lowering membrane thickness possesses a high potential to overcome the permeability-selectivity trade-off because of shorter pore channels. In the second part, we synthesize ultrathin polyamide membranes for efficient Mg^{2+}/Li^{+} separation by selecting a highly charged COF interlayer. These works may enlighten the development of a variety of membranes from polymers and organic framework materials towards ultra-permeable and selective separation of Li from concentrated Mg^{2+}/Li^{+} mixtures. More importantly, we hope the relationship among membrane structures, mass transport mechanisms and separation performances, from physical and chemical viewpoints, may shed some light on emerging ion transport mechanisms and have great implications for ion separation process intensification.

Publication List

1. Zhao, J.; You, X.; Wang, G.; Yuan, J.; Li, Y.; Yang, C.; **Zhang, S**.; Wang, X.; Zhang, R.; Wu, H.; Jiang, Z., Mix-charged polyamide membranes via molecular hybridization for selective ionic nanofiltration, Journal of Membrane Science, In press.
2. Long, M.; Yang, C.; You, X.; Zhang, R.; Yuan, J.; Guan, J.; **Zhang, S.**; Wu, H.; Khan, N.A.; Kasher, R.; Jiang, Z., Electrostatic enhanced surface segregation approach to self-cleaning and antifouling membranes for efficient molecular separation, Journal of Membrane Science, 2021, 638, 119689.
3. Zhang, R.; Zheng, Y.; Khan, N.A.; Gao, K.; **Zhang, S**.; Yang, C.; Guan, J.; Kasher, R.; Jiang, Z., Engineering dual-heterogeneous membrane surface with heterostructured modifier to integrate multi-defense antifouling mechanisms, Chemical Engineering Science: X, 2021, 11, 100103.

Design and synthesis nanoparticles with AIE feature for transparent mouse brain vascular imaging

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Abstract

Visualization of vascular networks plays an important role in understanding the pathologies of vascular dependent diseases. Compared to conventional vascular network visualization method, fluorescence imaging shows higher resolution, better sensitivity and offers multi-color detection capability. However, visualization and quantification of vascular system in whole organs with subcellular level resolution is limited due to poor light penetration in thick tissues. With the help of the developed optical clearing technique, the whole tissues could be imaged. To ensure high quality imaging, bright fluorophores resistant to the clearing process are highly desirable.

In the first work, a series of fluorogens with aggregation-induced emission (AIEgens) have been developed to address the problem of fluorophores retention in different optical clearing media. The emission of AIEgens could be easily adjusted by using different “Donor and Acceptor” units. Nanoparticles with surface functionalized amine groups (TSNs-NH2), were formed through self-assembly of AIEgens. These nanoparticles and polyacrylamide could form compact cross-linking hydrogels by covalent bonding, ensuring the stable and long-term fluorescence after continuous clearing procedures for lung tissue imaging.

In the second work, a new fluorophore with high photo-bleaching resistant in near-infrared window has been developed for thicker intact brain vascular imaging. Preliminary results suggested that these nanoparticles can be self-assembly to form nanoparticles and form hydrogels in 5 min. The performance of vascular imaging for intact brain is on-going.

In future, stable fluorophores within different biological windows will be developed for tissues with different thickness to further improve the quality of 3D whole body imaging.

Publication List

None

Multimodal Imaging Guided Photothermal Therapy for Targeted Brain Tumor Treatment

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Abstract

Phototherapy includes photodynamic therapy (PDT) and photothermal therapy (PTT), which mainly depends on phototherapeutic agents to generate heat or toxic reactive oxygen species (ROS). In the case of PDT, the photosensitizer absorbs light with appropriate wavelength and releases ROS, which results in oxidative damages to tumor cells. PTT utilizes a photothermal agent to convert the light into heat. The increased local temperature can directly lead to tumor ablation.

Herein, we aim to develop different nanoplatforms for tumor phototherapy. For the first project, we used a self-assembly strategy to prepare a diagnostic platform for photoacoustic imaging (PAI) guided PTT. A polymer named FTTBZ-PEG was synthesized and self-assembled into nanoparticles (NPs) for PAI and PTT. Compared with the normal NPs, in which FTTBZ was directly encapsulated in amphiphilic polymer DSPE-PEG, the FTTBZ-PEG NPs showed three strengths: first, it shows a weaker fluorescence but better photothermal effect. Second, due to ultrasmall size of FTTBZ-PEG NPs, a deeper penetration depth in tumor can be achieved. Additionally, the slightly negative zeta potential of FTTBZ-PEG can help the NPs escape from being captured by proteins in the blood, leading to a longer circulation.

In the second project, we synthesized an activable photosensitizer based on BODIPY core (denoted as BODIPYMal). BODIPYMal produces negligible ROS, however, after click reaction with Glutathione (GSH), the ROS generation ability is recovered. Given the fact that GSH is generally overexpressed in tumor cells, this GSH activated PDT strategy can selectively be activated in cancer cells with less side effect to normal cells.

Publication List

None

Molecular-Level Insight of Ligand Effect on the Electrophilicity of Au(I) in Au NCs for Electrocatalysis

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Abstract

While understanding the ligand effect on electronic structures of metal nanoclusters (NCs) is crucial for designing metal NCs based electrocatalysts with favourable adsorptions of reactants and/or intermediates, it remains challenging to identify the ligand effect on electronic structure of active-site metal atoms in metal NCs. In this work, we demonstrate the ligand effect on modulating the electronic properties of Au(I) in the motif of atomically precise Au_{25} NCs, by using para-mercaptobenzoic acid (pMBA), 6-mercaptohexanoic acid (MHA), and homocysteine (HCys)) protected $[Au_{25}(SR)_{18}]^-$ NCs (SR = thiolate ligands) as electrocatalysts for oxygen evolution reaction (OER). The various body structures of these ligands trigger a distinction in electron withdrawing ability, which has an impact on the electrophilicity of Au(I) in Au NCs. $[Au_{25}(pMBA)_{18}]^-$ NCs displayed best OER performance, with a decreased overpotentials by 90 mV at 10 mA/cm^2, higher turnover frequency (TOF) with 4.59 s^{-1} at the applied potential of 1.7 V and smaller Tafel slope of 62 mV/dec. This can be attributed to the influence of pMBA with a stronger electron withdrawing ability on more electrophilic of Au(I), providing active sites for nucleophilic adsorption of OH^- in the alkaline media. X-ray photo spectroscopy (XPS) suggests a profound electron transfer from Au(I) to pMBA via the connected sulphur atoms for $[Au_{25}(pMBA)_{18}]^-$ NCs. The Tafel slope and the *in situ* Raman spectroscopy indicate the contribution of pMBA to the formation of Au-O-OH on the surface of $[Au_{25}(pMBA)_{18}]^-$ NCs accounts for the OER performance enhancement. The mechanistic insights reported here can add to the acceptance of atomically precise metal NCs as effective electrocatalysts for OER.

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1. Liu, Z.; Wu, Z.; Yao, Q.; Cao, Y.; Chai, O. J. H.; Xie, J., Correlations between the fundamentals and applications of ultrasmall metal nanoclusters: Recent advances in catalysis and biomedical applications. Nano Today **2021**, 36, 101053.
2. 2.Wu, Z.; Yao, Q.; Liu, Z.; Xu, H.; Guo, P.; Liu, L.; Han, Y.; Zhang, K.; Lu, Z.; Li, X.; Zhang, J.; Xie, J., Multiscale Assembly of [AgS4] Tetrahedrons into Hierarchical Ag–S Networks for Robust Photonic Water. Adv. Mater. **2021**, 33 (8), 2006459.
3. 3.Li, C.; Chai, O. J. H.; Yao, Q.; Liu, Z.; Wang, L.; Wang, H.; Xie, J., Electrocatalysis of gold-based nanoparticles and nanoclusters. Materials Horizons 2021, 8 (6), 1657-1682.
4. M Zhu, Q Yao, Z Liu, B Zhang, Y Lin, J Liu, M Long, J Xie* Surface Engineering Assisted Size and Structure Modulation of Gold Nanoclusters by Ionic Liquid Cations. Angew. Chem. Int. Ed. **2021**, accepted manuscript.

Revealing the composition-dependent structure evolution fundamentals of bimetallic nanoparticles through the inter-particle alloying reaction

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Abstract

Alloy nanoparticles represent one of the most important metal materials, finding increasing applications in diverse fields of catalysis, biomedicine, and nano-optics. However, the structure evolution of bimetallic nanoparticles in their full composition spectrum has been rarely explored at the molecular and atomic level, imparting inherent difficulties to establish reliable structure-property relationship in practical applications. Here, through the inter-particle reaction between $[Au_{44}(SR)_{26}]^{2-}$ and $[Ag_{44}(SR)_{30}]^{4-}$ nanoparticles or nanoclusters (NCs), which possess the same number of metal atoms, but different atomic packing structures, we reveal the composition-dependent structure evolution of alloy NCs in the alloying process at the molecular and atomic level. Particularly, inter-cluster reaction can produce three sets of Au_xAg_{44-x} NCs in the full composition spectrum (i.e., x = 1-43), and the structure of Au_xAg_{44-x} NCs evolves from the Ag-rich $[Au_xAg_{44-x}(SR)_{30}]^{4-}$ (x = 1-12), to the evenly mixed $[Au_xAg_{44-x}(SR)_{27}]^{3-}$ (x = 19-24), and finally to the Au-rich $[Au_xAg_{44-x}(SR)_{26}]^{2-}$ (x = 40-43) NCs, with the increase of Au/Ag atomic ratio in the NC composition. The intermediate $[Au_xAg_{44-x}(SR)_{27}]^{3-}$ NCs likely possess a heterodimeric structure inheriting from the two parent NCs of $[Au_{44}(SR)_{26}]^{2-}$ and $[Ag_{44}(SR)_{30}]^{4-}$. In addition, leveraging on the real-time electrospray ionization mass spectrometry (ESI-MS), we reveal the different inter-cluster reaction mechanisms for the alloying process at sub-3-nm regime, including partial decomposition-reconstruction and metal exchange reaction. The molecular-level inter-cluster reaction demonstrated in this study provides a fine chemistry to customize the composition and structure of bimetallic NCs in their full alloy composition spectrum, which will greatly increase the acceptance of bimetallic NCs in both basic and applied research.

Publication List

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2. Zhu, M.; Yao, Q.; Liu, Z.; Zhang, B.; Lin, Y.; Liu, j.; Long, M.; Xie, J., Surface Engineering Assisted Size and Structure Modulation of Gold Nanoclusters by Ionic Liquid Cations. Angew. Chem. Int. Ed. **2021**, accepted manuscript.

Exquisitely Functionalize the Surface of $Au_{25}(SR)_{18}$ via a Two-Phase Ligand Exchange Method

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Abstract

Gold nanoclusters (Au NCs) are a kind of ultra-small nanoparticles with a diameter of less than 2 nm. The strong confinement effect endows Au NCs distinct molecular-like properties, such as enhanced photoluminescence, discrete electronic structures and redox behaviors, and thus potential in various applications such as catalysis, sensors, bio-imaging and so on. In all these applications, ligands on the surface of Au NCs play an important part as the first layer to have an interaction with the exterior environment (i.e., solvent, reactant, cells and so on.). However, how to controllably, effectively and high yield functionalize this surface layer of Au NCs is still a tall order, which limits not only the practical applications but the fundamental understandings of Au NCs. To solve this problem, we developed a two-phase ligand exchange method to surface functionalize the hydrophilic Au NCs. By regarding the ligand exchange reaction and etching reaction as two parallel reactions that happened after mixing Au NCs and organic ligands, we introduced another phase in the conventional ligand exchange reaction. This two-phase system will impose phase transfer resistance between Au NCs and exterior ligands during the ligand exchange process, which can inhibit the ligand exchange rate, making the surface functionalization process more controllable. The results show that this method can effectively exchange 93.3% ligands on the surface of Au NCs with yield of 94%. What's more this two-phase ligand exchange method show broad accessibility to almost all organic thiol ligands (i.e., aromatic and alkane ligands and ligands with various functional groups), shedding light on tailoring the physiochemical properties of Au NCs and functionalize Au NCs for more 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**, 125 (1), 489.
2. Zhang, B., Chen, J., Cao, Y., Chai, O. J. H., Xie, J., Ligand Design in Ligand-Protected Gold Nanoclusters. Small **2021,** 17, 2004381.
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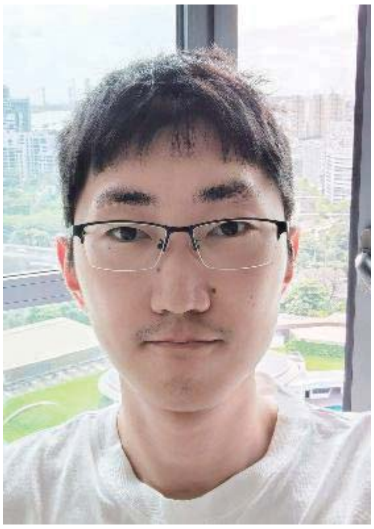
4. Zhu, M.; Yao, Q.; Liu, Z.; Zhang, B.; Lin, Y.; Liu, j.; Long, M.; Xie, J., Surface Engineering Assisted Size and Structure Modulation of Gold Nanoclusters by Ionic Liquid Cations. Angew. Chem. Int. Ed. **2021**, accepted manuscript.

Photoexcitation Induced Phonon Coupled Non-Radiative Energy Dissipation in Organic Charge Transfer Crystals



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Abstract

Non-radiative energy dissipation is an inevitable process in photoexcited organic materials, which deteriorate photoluminescence and photovoltaic performance despite preferred by photothermal applications. Therefore, the understanding on non-radiative energy dissipation process can provides fundamentals to screening and design high performance organic materials for photoluminescence, photovoltaic, as well as photothermal applications. To imitate the ensemble of mostly used photo excitable functional organic materials with charge transfer characteristics, organic charge transfer crystals as long-range ordered donor acceptor aggregates, provide an adequate platform for the research of photoexcitation and relaxation dynamics. In this presentation, we report our recent study on non-radiative energy dissipation in a series of organic small molecular charge transfer crystals. In particular, we show the key effect of the generation of charge transfer excitons on the producing of low frequency phonon modes which dominate the deexcitation process. Furthermore, by focusing on spatial electron populations and molecular vibration modes of ground state and excited state, we analyze the process of the formation and the coupling of charge transfer excitons and low frequency phonons. Finally, we make a conclusion on the photoexcitation induced phonon coupled non-radiative energy dissipation in organic charge transfer crystals and describe some future work and perspectives.

Publication List

None

Novel NIR-Emitting Halide Perovskite Single Crystals

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Abstract

Halide perovskites have rapidly become star materials since their birth. Their merits including tunable emission color, large absorption cross-section, ease to be synthesized, and high defect tolerance have witnessed their fruitful applications.

When perovskites are used as luminescent materials, however, their emission color can almost only be tuned within visible window. Among perovskite families, only $FAPbI_3$ and $CsSnI_3$ can give NIR emission. However, they are extremely unstable even in ambient conditions owing to the easy decomposition of FA^- or oxidation of Sn^{2+}. Although researchers have successfully doped lanthanide metals into halides to obtain NIR light, the energy transfer efficiency from perovskite hosts to emission centers are rather low, which makes them hard to be applied in reality. Moreover, lead in these compounds is very harmful to nature environment and human bodies. Therefore, it is of high impact to develop novel halide perovskites that possess the advantages of efficient NIR emission, stability, and non-toxicity.

Here, we succeeded in developing two unreported NIR-emitting single crystals. Not only they can give NIR emission approaching to wavelength of 1000 nm, but also are toxicity-free with high stability against polar solvent, UV/X-ray radiation and high temperature. The multiple emission mechanisms are explored and the application in night vision/tissue imaging are demonstrated.

Publication List

1. Luminescence enrichment in perovskite-lanthanide composites: Complexity and complementarity, Zhuang L.; Xian Q.; Xiaogang L. *Handbook on the Physics and Chemistry of Rare Earths.*

Low-dimensional Halide Perovskites with Organic Functional Molecule Layers for X-ray Detection

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Abstract

The three-dimensional (3D) organic–inorganic halide perovskites have shown great potential of the use in X-ray imaging and other photoelectric devices. Nevertheless, intrinsic instability and ion migration in 3D perovskites can lead to material degradation and hinder large-scale commercial applications. Dion–Jacobson (DJ) phase perovskites, as a kind of two-dimensional (2D) materials, have demonstrated to be more stable than 3D counterparts for X-ray detection because of the isolation between two inorganic metal halide octahedra layers by large organic cations. However, these spacing cations can also promote the formation of quantum well superlattices which may reduce the carrier mobility. Herein, we develop a series of perylenetetracarboxylic diimide (PDI) derivatives to prepare DJ phase perovskite. As the electron acceptor, PDI derivatives are able to improve the carrier mobility of the layered perovskites. Moreover, according to the fluorescence spectra and transient absorption spectra results, the energy transfer process from inorganic layers to organic layers can improve the red-light emission of PDI molecules significantly. These findings demonstrate a new and promising strategy to develop high performance DJ phase perovskites for X-ray detection and other photoelectric applications.

Publication List

None

Three-dimensional Carbon as Inorganic Filler toward Self-healing Composite Solid-Sate Electrolyte for All Solid-State Lithium Metal Battery

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Abstract:

Although Poly(ethylene oxide) (PEO)-based electrolyte has many intrinsic advantages, e. g., good flexibility and film-forming property, its low lithium ionic conductivity and poor electrochemical stability impede its practical application. Here, an effective and plain strategy is proposed to produce self-healing composite solid-sate electrolyte (CSSE) for incorporating three-dimensional carbon (3D C) which is prepared with using salt-assisted method into PEO matrix with conventional aqueous mixing approach. Such excellent 3D structure of 3D C not only provides continuous transfer ways for lithium cations but also offers amounts of sites for interacting with PEO chains, promoting the self-healing process. As a consequence, the CSSE containing 2 wt% 3D C with high ionic conductivity of 5.8 × 10-4 S cm-1, long-term electrochemical stability (3000 h cycles for lithium symmetric battery at 0.1 mA cm-2, and 400 cycles for LiFePO4//Li battery at 1 C) is achieved.

Publication List

None

Application of Molecular Dynamic Simulation in Functional Materials

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Abstract:

Since the introduction of commercial Li-ion batteries in 1991, we have witnessed tremendous development in portable electronic devices, and the recent emergence of electric vehicles promises to revolutionize personal transportation too. The inherent limitations of Li-ion chemistry make it unlikely, however, that this type of battery can meet the growing demand for energy density, and it is now widely accepted that battery chemistries beyond Li-ion need to be developed.

As is known to all, the principle behind those outstanding-performance battery is crucial. DFT(Density Functional Theory) is the most widely used method to show the detailed mechanism, indeed it opens our field of vision and gives lots of guidance during the material structure design. However, because of the huge calculation work load, DFT always suffer from the limit of atom numbers in the system and the long calculation time. Molecular Dynamic Simulation(MDS) was first developed and used by Metropolis, Rosenbluth and Teller in 1959, National laboratory of America. Because of the ready made potential file and the permission to simulate Van Der Waals system, it can simulate very large system and can do a lots of dynamic simulations. In the last decades, people usually use DFT to calculate absorption energy or the reaction between two atoms, they focus on the atom level but ignore the macro level mechanism. Here, creatively, we successfully use Molecular Dynamic Simulation to reveal the principle behind the high performance of our Sodium ion battery, and use MDS to predict the performance in other battery system. In another work, we also use MDS to simulate the hot-press process to reveal the reason why we can synthesize such performance-stable self-standing electrode material.

Publication List

1. B.Chen, J. Ding, X. Bai, H. Zhang, M. Liang, S. Zhu, C. Shi, L. Ma, E. Liu, N. Zhao, F. He, W. Zhou, C. He. Adv. Funct. Mater. 2021, 2109899

MOF-based materials for electrocatalytic applications

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Abstract

MOFs are formed by coordination bonds between organic ligands and metal atom nodes with periodic structural units. Due to their structural characteristics, MOFs can 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.

However, MOF systems still suffer from low mass permeability, poor conductivity and blockage of active metal centres by organic ligands, dramatically limiting their utilization as electrocatalysts. Ultrathinning MOFs into two-dimensional nanosheets can be an effective strategy to acquire MOF-based high-performance electrocatalysts, but they are not enough.

Here, we report ultrathin MOF derivatives as efficient electrocatalysts. Our bimetal–organic framework derivatives show good electrocatalytic performances in OER, HER and ORR. Based on these electrocatalytic performances, ultrathin MOF derivatives have potential applications in overall water splitting and zinc-air batteries. The bimetal-organic framework derivatives have potential applications in CO2RR.

Publication List

None

Machine learning aided synthesis of polyamide nanofiltration membrane with high selectivity and permeability

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Abstract

Interfacial polymerization (IP) is a popular technique to fabricate state-of-the-art nanofiltration (NF) membranes. However, due to the inherent limitations of the polyamide chemistry, as well as the limiting understanding of IP reaction mechanisms, existing NF membrane fabrication processes are largely empirical and lack molecular-level design, leading to the formation of a selective layer with uncontrolled characteristics. Therefore, tailoring nanofiltration membranes with both high selectivity and permeability remains a technical challenge for current IP methods. Herein, we compiled a data set constituted by 114 newly synthesized NF membranes from our lab and trained the machine learning (ML) models for the first time to correlate the IP fabrication conditions with membrane performance. Among six competing models, artificial neural network (ANN) showed the best performance on the training and testing data set with highest the average R^2 scores of 0.98 and 0.92, respectively. Further, the ANN model showed high prediction accuracy with the mean absolute percentage error (MAPE) values less than 7% in terms of the uncharted data points. To gain more insights into the complicated IP process, the influence of the membrane fabrication conditions and their mutual effect on the membrane performance were discussed using partial dependence plot analysis. Ultimately, the ANN model was used to identify the membrane fabrication conditions that improve solute selectivity and permeability of existing membranes. The optimized membrane showed high NaCl/$MgCl_2$ selectivity of 30.02 and pure water permeability of 15.66 L m^{-2} h^{-1} bar^{-1}, which outperforms all the data points in the dataset and exceeds the separation performance upper bound of state-of-the-art polyamide membranes. Our work suggests that machine learning is a promising future platform for high-performance membrane synthesis.

Publication List

None.

Anion Transport in Functional Covalent Organic Framework: A Molecular Simulation Study

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Abstract

Covalent organic framework (COF) has exhibited great potential in making membranes. The use of side chains to modify the chemical environment of the pore surface is used by more and more researchers, and COF membrane has excellent performance in ion rapid transport. However, the transport mechanism of ions in the COF membrane and their pattern of movement are rarely studied. Using molecular dynamic (MD) simulation method, we investigate chloride ion (Cl-) transport through a series of side-chain quaternized frameworks (COF-QAs) with different spacers. We herein demonstrate a flexible COF membrane modeling method that can match the experimental results more accurately, and demonstrates the ion transport mechanism in the membrane through quantitative analysis. The electrostatic attraction and steric hindrance are important reasons that affect ion transport. The charges on the functional group will influence the hydration layer of the ions and the density distribution of the ions in the channels. The main transport mode of ions is the passing between different functional groups. These findings and understandings on ion transport mechanisms can also be applicable to ion separation and osmotic energy conversion membranes. This work could provide guidelines for the experimental design of Ionized COF membrane.

Publication List

None

Atomically Precise Robust Gold Nanoclusters as Peroxidase Mimics for tandem Catalysis

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Abstract

Gold nanoclusters have received great attention in the field of catalysis due to their distinctive properties, such as ultrasmall sizes, large surface area, well-defined structure, and absolute monodispersity. However, the instability of gold nanoclusters is a big challenge which largely limits their applications. Therefore, the aim of this work is to design robust gold nanoclusters through ligand engineering. Our work proved that the Au_{15} NCs protected by one amino acid derivative possessed ultrahigh pH stability and antioxidant stability in comparison with Au_{15} NCs protected by other ligands. Considering that the ligand-core structure of Au_{15} NCs is similar to the tertiary structure of enzymes, we anticipate that Au_{15} NCs can be utilized as potential enzyme-mimics. One typical enzymatic reaction was carried out to verify the enzyme-like behaviors of Au_{15} NCs. The results demonstrated that Au_{15} NCs can catalyze the oxidation of TMB in the presence of H_2O_2, just like peroxidase. Therefore, Au_{15} NCs might be used as the potential enzyme substitutes and applied in the multienzymatic cascade reactions for biosensing, colorimetric assay, manufacture of high-value chemicals and pharmaceuticals, etc.

Publication List

None

Selenium-Containing AIEgens for Combined Immunotherapy and Photodynamic Therapy

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Abstract

Synergistic therapy has emerged as a promising new approach for cancer treatment. However, the optimal ‘1+1>2’ therapy effect of clinically available drugs have been limited until recently, and the detailed understanding of the effect of different therapy strategies on specific molecular pathways in cancer cells need to be improved, which can help to optimize the synergistic antitumour efficiency. Herein, we synthesize a kind of near-infrared (NIR) emissive fluorescent molecules with aggregation-induced emission (AIE) characteristics and theranostic functions, which is able to specifically target and aggregate on the cell membrane and realize the ultrafast ‘light up’ bioimaging and photodynamic therapy (PDT). In addition, through incorporating the nitrogen heterocyclic carbene (NHC)-selenium unit into this AIE photosensitizer, selenide can be oxidized to seleninic acid by the singlet oxygen produced in the PDT process, which suppresses the expression of human leukocyte antigen E (HLA-E) on the cancer cell membrane, thus activating the immune attack of NK cells. In this way, this work introduces a new synergistic therapy strategy combined with cancer photodynamic therapy and immunotherapy by a simple but effective method.

Publication List

None

In-Situ Synthesized Polymer Photosensitizers for Cancer-Cell-Activated Photodynamic Therapy

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Abstract

Photodynamic therapy (PDT), which uses photosensitizers (PSs) along with light to kill cancer cells, is one of the most promising approaches to treat cancer since it is spatiotemporally precise, readily controllable, non-invasive, and with low side effects. There is an increasing demand for more effective PSs that could cause maximized phototoxic damage on tumor with minimized side effects in healthy cells. Herein, a new strategy is reported to achieve selective in-situ synthesis of polymer PSs inside cancer cells through the use of MOF-199, a Cu(II) carboxylate-based metal–organic framework (MOF), as the nanocarrier for precise delivery of two monomers and a Cu(I) catalyst source for in-situ click reaction to form polymers. The in-situ intracellularly synthesized polymer PS, as an efficient image-guided PDT agent, can kill cancer cells on site under light irradiation, diminishing normal cell phototoxicity. Concomitantly, it showed much higher photosensitization efficiency in singlet oxygen ($^1O_2$) production than their monomers or oligomer counterparts due to polymerization-enhanced photosensitization.

Publication List

None

Organic Emitters for Device and Biological Applications

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Abstract

Nitric oxide (NO), as a signal transduction molecule with biological activity in the body, plays an important physiological function in the prevention and treatment of chronic diseases. Compared with other preparations, the endogenous existence of NO and the characteristic of transforming into harmless ions after 6 seconds of action determine that it can not only exert efficacy, but also minimize toxic and side effects. Therefore, NO is considered to be an ideal drug. The strategy based on increasing the production of NO for the prevention and treatment of cardiovascular diseases and tumors has become a research hotspot in recent years.

To avoid the problem of uncontrollable release when using NO gas molecules for treatment, many researchers use carriers (such as liposomes) to combine NO gas or NO donor molecules, delivering NO to target tissue. However, the loading of NO gas is difficult, the NO donor molecules (such as NONOate and RSNO) are unstable, and the carrier loading efficiency is low. Therefore, we use light-responsive N-nitrosamines as the NO-releasing element to prepare light-responsive NO-releasing molecules. The responsive NO release material increases the content of NO and realizes the controlled release of NO in time and space. In the future, we would like to learn the role of materials in the treatment of disease.

Publication List

None

Design and Synthesis D-A-D Type Near-infrared II Fluorescent Dye Based on Strong Acceptor for PDT/PTT Cancer Therapy

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Abstract

Modern biomedical imaging technology is an indispensable tool in clinical diagnosis and treatment evaluation. It can observe pathological and physiological events related to human diseases non-invasively, highly sensitively and specifically. In the past few decades, organic fluorescent dyes have attracted much attention due to the advantages of easy modification of functional groups, adjustable structure, and non-invasiveness. However, traditional fluorescent dyes are usually accompanied by shorter emission wavelengths, which are prone to problems such as large background fluorescence interference and small tissue penetration depth in practical applications. The design and development of fluorescent probes with near-infrared I/II (NIR-I; 700-900 nm, NIR-II, 1000-1700 nm) solves this problem well. For now, there are few reports on the design of a new type of NIR-II fluorescence fluorophore. To further expand the system with NIR emission AIEgens and broaden the absorption and emission spectra of AIE target compounds, in this study we use strong electron-drawing core 2,2'-(9,10-anthracenediylidene) -bis-propanedinitrile (TCNAQ) to construct the AIE fluorescent dye with NIR-I/II emission. The series of compounds can be employed for PAI and PL imaging. Besides, TPA-TCNAQ shows good photothermal property, which can be used for phorothermal cancer therapy.

Publication List

None

Composition-dependent catalytic selectivity of Au_xAg_{25-x} alloy nanoclusters for oxygen reduction reaction

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Abstract

Oxygen reduction reaction (ORR) occurs at the cathode of some electrochemical systems like fuel cells and metal-air batteries, reducing oxygen to water or hydrogen peroxide. At present, many kinds of catalysts have been developed to improve the efficiency of the system or to produce hydrogen peroxide in a green manner. However, the relationship between the catalyst structure and its selectivity has not been established. As a unique class of metal nanoparticles, metal nanoclusters (NCs) have well-defined molecular formula and structure. In addition, the composition of NCs can be finely tailored, which provides us a good platform to understand their structure-property correlations. Here, we prepared a full spectrum of alloy metal NCs, $Au_xAg_{25-x}(MHA)_{18}$ (MHA = 6-mercaptohexanoic acid) with x = 0-25 by co-reduction and metal exchange method, and investigated their composition-dependent electrocatalytic ORR performance. The results showed that with the doping of Ag, the number of electron transfer gradually increased from 2.1 for $Au_{25}MHA_{18}$ to 3.9 for $Ag_{25}MHA_{18}$, indicating that the reduction product gradually changed from hydrogen peroxide to water. This may be because Ag has a stronger adsorption for O_2, so it will take a dissociation pathway to generate water. Density functional theory calculations will be carried out to verify this. This study suggests that alloy metal NCs will become promising to understand the composition-dependent electrocatalytic properties.

Publication List

None

Synthesis of AIE-Type Luminescent Metal Nanoclusters through Etching Reaction

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Abstract

Metal nanoclusters are ultrasmall particles with a diameter of about 1 nm. They feature interesting molecule-like properties, such as strong luminescence, which can be used to construct luminescent probes in various applications, including bioimaging and biosensing. Bottom-up synthesis is a general pathway to synthesize luminescent metal nanoclusters, especially those with aggregation-induced emission (AIE) properties (or so-called AIE-type luminescent metal nanoclusters). There are a number of successful attempts in synthesizing AIE-type luminescent metal nanoclusters through the bottom-up route, however, the types of luminescent metal nanoclusters are rather limited. Therefore, there is a pressing need to develop new synthetic routes to produce high-quality AIE-type luminescent metal nanoclusters, and the top-down method may provide another efficient way to generate luminescent metal nanoclusters. In this work, we use $Au_{25}(MHA)_{18}$ as a model nanocluster and utilize the etching reaction to systematically explore etching products and their corresponding luminescence properties. We have identified three main reaction processes in the entire etching process, which can generate new metal nanocluster species with various luminescence properties. The etching reaction (or top-down synthesis) will provide a good platform for the generation of new luminescent metal nanocluster species.

Publication List

Chen, T.; **Lin, H.**; Cao, Y.; Yao, Q.; Xie, J., Interactions of Metal Nanoclusters with Light: Fundamentals and Applications. Adv. Mater. 2021, 2103918.

Chemical Reaction Kinetics of Gold Nanoclusters for High Scale Synthesis

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Abstract

Reaction kinetics is a quantitative measurement of the impact on the chemical reaction for different variables such as concentration and temperature. Ligand-protected gold nanoclusters are ultrasmall gold nanoparticles that are in the intermediate state between the single atom and plasmonic particles. They have a definite molecular formula with well-defined molecular structure and possesses molecular-like physical and chemical properties. Due to these unique features, nanoclusters have great potential in various applications fields, such as photocatalysts, electrocatalysis, bioimaging, and chemical sensors. Understanding the reaction kinetics will not only help with faster and higher-yield synthesis, but also increase the application viability of gold nanocluster. For this work, $Au_{25}(pMBA)_{18}$ is used as the model nanocluster for the exploration of reaction kinetics, due to its easy preparation, high stability, and long research history.

Publication List

none

High order, non-Hermitian, Floquet Topology and knot theory

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Abstract

Valence and conduction bands in nodal loop semimetals (NLSMs) touch along closed loops in momentum space. If such loops can proliferate and link intricately, NLSMs become exotic topological phases, which require nonlocal hopping and are therefore unrealistic in conventional quantum materials or cold atom systems alike. We show how this hurdle can be surmounted through an experimentally feasible periodic driving scheme. In particular, by tuning the period of a two-step periodic driving or certain experimentally accessible parameters, we can generate arbitrarily many nodal loops that are linked with various levels of complexity. Furthermore, we propose to use both a Berry-phase related winding number and the Alexander polynomial topological invariant to characterize the fascinating linkages among the nodal loops. We present a class of exotic Floquet topological phases that has hitherto not been proposed in any realistic setup.

Publication List

(First or co-first author papers followed by co-author papers)

None

Nanoscale NMR sensor based on NV centers in diamond

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Abstract

Nanoscale NMR sensors are desired in many research fields like drug development due to their small detectable volume. NV center is a kind of defects in diamond. It can sense local magnetic field information and express it into fluorescence information. The fluorescence information can be detected using different microwave sequences. Among these sequences, Coherently Averaged Synchronized Readout (CASR) sequence is the most advanced one which offers Fourier limited resolution. We used this sequence to detect an AC magnetic field generated by current we applied and reached arbitrary high frequency resolution of that signal.

Currently, the biggest limitation of NV center is its sensitivity. Compared with other competitive techniques whose sensitivity reach 10^{-15} Tesla, the record sensitivity of NV center only reaches 10^{-12} Tesla. This discrepancy corresponds to 10^{6} times measurement time difference. We are trying to analyze the factors that limit the sensitivity of NV sensors and improve the sensitivity of our NV sensor.

Publication List

None

Bulk Photovoltaic Effect in Chiral Perovskite for Self-Powered Circularly Polarized Light Photodetector

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Abstract

Circularly polarized light (CPL) detection is necessary in many fields, including quantum communication, security monitoring, and spin optical information, etc. Circularly polarized light photodetector (CPL PD) is an optoelectronic device that can directly convert CPL into different electrical signals. Recently, chiral halide perovskites are reported to have great potential in fabricating high-performance CPL PDs due to their good CPL absorption and excellent photoelectric properties. Compared with CPL PDs based on organic chiral semiconductors or metal metamaterials, these chiral perovskites-CPL PDs behave promising CPL distinction, higher sensitivity, and faster response speed. Most importantly, the apparent bulk photovoltaic effect in chiral perovskites make the self-powered CPL PDs possible, which improve their device-integration and then widen their applications in flexible and wearable electronics in future. In this report, the working principle, key parameters, and research progresses of chiral perovskite-CPL PDs and self-powered devices have been summarized.

Publication List

None

The Effect of Anion Impurities in Electrolyte for Electrochemical CO2 Reduction

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Abstract:

With the increasing temperature all over the world, which is caused by the greenhouse gases, decreasing CO2 concentration has attracted more and more attention. Electroreduction of CO2 into high-value fuel is one of promising ways. Until now, copper and copper-bearing materials are the unique catalyst that can reduce CO2 into C2 and C2+ products. However, applying this technology to industrial CO2 sources requires an understanding of the influence of impurity ions in the electrolyte solution on the CO2 reduction reaction. Although many studies have been conducted on electrode materials, we already know that the electrolyte solution also plays a non-negligible role in the entire catalysis process, and the electrolyte and electrode surface are a very critical factor. As we all know, there are four major anions in seawater: Cl^-, SO_4^{2-}, CO_3^{2-} (including HCO_3^-), and Br^-. In order to provide a reference for future industrial carbon dioxide energy conversion and have a deeper understanding of the CO2 reduction process, here, we use copper as a model catalyst and studied the effects of sulfate on the catalytic performance.

Publication List:

None.

MOFs modified copper oxide materials for CO2 electrochemical reduction reaction

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Abstract:

With the development of industries, a huge concern has been risen on the mass release of CO2, which caused a lot of problems like greenhouse effect and the global climate change. In fact, CO2 can be used as raw material to synthesis some useful chemicals by electrochemical reduction reaction. In CO2RR system, catalysts always play a crucial role during the process. Cu is considered the only metal that can catalyze CO2 into C2+ products. However, the moderate binding strength of various intermediates has caused the poor selectivity towards specific chemicals on the copper surface.

MOFs is a good choice to modify copper oxide materials because inherent pore confinement properties could induce local CO2 concentration enhancement and restrain HER reaction. Controllable pore size, ligand and the open metal sites offer avenues to adjust the metal site environment and optimize catalytic performance. Here, we explore to prepare the copper oxide encapsulated in MOF material, which shows better electrocatalytic performance for C2+ products.

Publication List

None

Workshop Schedule

8th Jan 2022: NUS-TJU PhD Workshop **Center 3: Energy Storage and Electrocatalysis** **Symposium Chair: Chen Wei**				
		Presenter	**Title**	**Supervisor**
Session Chair: Wang Meng				
Morning	9:00-9:20	Lu Haotian	High-dielectric coating for uniform lithium deposition in lithium metal batteries	Yang Quan-hong &Chen Wei
	9:20-9:40	Wang Lu	Ultrathin Silicon-coupling agent-based protective coating for stable Zn anodes	Yang Quan-hong & Loh Kian Ping
	9:40-10:00	Liu Yuan	Probing Fluorination Promoted Sodiophilic Sites with Model Systems of F_{16}CuPc and CuPc	Chen Wei
	10:00-10:20	Luo Yani	Multi-functionalization of a newly additive for the improved electrochemical performance of the aprotic Li-O_2 batteries	Chen Wei
	10:20-10:40: Break			
	Session Chair: Wang Meng			
	10:40-11:00	Wang Feifei	Phosphorene Directed Growth of 1D NiS Nanowire Arrays for Oxygen Evolution Reaction	Yang Quan-hong & Lu Jiong
	11:00-11:20	Da Yumin	Pt-Ni dual atom catalyst with mass activity 21-fold higher than commercial Pt/C towards efficient hydrogen evolution	Hu Wenbin & Chen Wei
	11:20-11:40	Jin Tengyu	Two-Dimensional Reconfigurable Electronics Enabled by Asymmetric Floating Gate	Chen Wei
Lunch Break				
		Presenter	**Title**	**Supervisor**
Session Chair: Yang Haotian				
Afternoon	14:00-14:20	Yang Haotian	Construct a high-performance Li-S battery by tuning the coordination environment of Co catalyst	Yang Quan-hong &Chen Wei
	14:20-14:40	Sun Buwei	Dual Atom Catalyst for Oxygen Reduction Activity in Zinc–Air Batteries	Hu Wenbin & Liu Xiaogang
	14:40-15:00	Jiang Chonglai	Modification of the Interface between Lithium Anode and Garnet Electrolyte	Chen Wei
	15:00-15:20	Wang Meng	Tailoring Li_2O_2 Growth Route by Crystal Facet Engineering in Bifunctional Photo-assisted Li-O_2 Battery	Chen Wei
	15:20-15:40: Break			
	Session Chair: Yang Haotian			
	15:40-16:00	Cui Baihua	Defect-rich Nanocatalysts fabricated by Thermal Shock for the Hydrogen Evolution Reaction	Hu Wenbin & Chen Yanan & Chen Wei
	16:00-16:20	Zuo Yong	Silly putty-like materials for flexible/wearable electronics	Hu Wenbin & Liu Xiaogang
	16:20-16:40	Shi Jiwei	Fabrication of Single-atom Catalyst for Organic Coupling Reactions	Yang Quan-hong & Lu Jiong
	16:40-17:00	Wang Yihe	Evolution of low-dimensional Phosphorus allotropes on Ag(111)	Chen Wei & Huang Yuli

High-dielectric coating for uniform lithium deposition in lithium metal batteries

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Abstract

Lithium metal battery is one of the most promising candidates for next-generation high energy density devices owing to the high specific capacity and low electrochemical potential of lithium metal anode. However, lithium dendrite growth resulting from nonuniform growth causes low Coulombic efficiency, poor cycling stability, and even safety problems to hinder the commercial application of lithium metal batteries. To solve this problem, we propose a strategy to suppress the electric field gradient by coating a high-dielectric film on the lithium metal anode. The uniform electric field gradient can cause uniform ion distribution, then promote a uniform lithium deposition.

This study offers a new strategy for the development of dendrite-free metal anode technology.

Publication List

1. Zhou, S., Wang, Y. P., **Lu, H. T.**, Zhang, Y. F., Fu, C. Y., Usman, I., Liu, Z. X., Feng, M. Y., Fang, G. Z., Cao, X. X., Liang, S. Q., Pan, A. Q., Anti-Corrosive and Zn-Ion-Regulating Composite Interlayer Enabling Long-Life Zn Metal Anodes. Adv. Funct. Mater. 2021, 31, 2104361.

Ultrathin Silicon-coupling agent-based protective coating for stable Zn anodes

Wang Lu, Loh Kian Ping, Quan-hong Yang
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Abstract

The metallic zinc (Zn) has been regarded as a promising anode material towards an aqueous Zn-ion battery with high energy density, however, which cyclability are serious hindered by dendrite formation and side reactions during Zn-electrodeposition and -stripping. Numerous studies have proved that forming and keeping a stable and zincophilic anode-electrolyte interface are vital to ensure high stability of Zn anodes. Here, an ultrathin silane coupling agent (APTES) based protective layer, which incorporated on the surface of Zn anode through covalent bond, have been proved as an effective strategy to solve the above issues. Benefit from the APTES coating, the modified Zn anodes deliver a stable cycling nearly 3000 h at 0.5 mA cm^{-2} and 0.5 mAh^{-2} and more than 1500 h at 10 mA cm-2 and 1 mAh cm^{-2} as well as a much-improved capacity retention ratio for Zn//ZVO full batteries.

Publication List

None

Probing Fluorination Promoted Sodiophilic Sites with Model Systems of F_{16} CuPc and CuPc

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Abstract

Sodium metal batteries (SMBs) are receiving broad attention due to the high specific capacity of sodium metal anode and its abundance on earth. However, the growth of dendrites results in poor battery performance and severe safety problems, inhibiting the commercial application of SMBs. In order to stabilize sodium metal anodes, various methods have been developed to optimize the solid electrolyte interphase (SEI) layer and adjust the electroplating/stripping behavior of sodium. Among them, developing anode host materials and adding electrolyte additives to build a protective layer are promising and convenient ways. However, the understanding of the interaction process between sodium metal and those organic materials is still limited, which is essential for the rational design of advanced anode hosts and electrolyte additives. In this work, we use copper(II) hexadecafluorophthalocyanine (F_{16}CuPc) and copper(II) phthalocyanine (CuPc) as model systems to unravel the sodium interaction with polar functional groups by *in-situ* photoelectron spectroscopy and density functional theory (DFT) calculations. It is found that sodium atoms prefer to interact with the inner pyrrolic nitrogen sites of CuPc, while they prefer to interact with the outer aza bridge nitrogen atoms owing to Na-F interaction at Na/F_{16}CuPc interface. Besides, for both organic molecules, the central Cu(II) ions are reduced to Cu(I) ions by charge transfer from deposited sodium. The observed fluorination promoted interaction process of sodium in organic materials shed lights on the design of functional interfaces in host materials and anode protective layers for sodium metal anodes.

Publication List

1. Dai WR, **Liu Y**, Wang M, Lin M, Lian X, Luo YN, Yang JL, Chen Wei*. Monodispersed Ruthenium Nanoparticles on Nitrogen-Doped Reduced Graphene Oxide for Efficient Lithium-Oxygen Battery. ACS Applied Materials & Interfaces 13, 19915 –19926 (2021).
2. Lian X, Ma ZR, Zhang ZH, Yang JL, **Liu Y**, Gu CD, Guo R, Wang YN, Ye X, Sun S, Zheng Y, Ding HH, Hu, J, Cao X, Mao HY, Zhu JF, Li SZ, Chen Wei*. Alkali Metal Storage Mechanism in Organic Semiconductor of Perylene-3, 4, 9, 10- Tetracarboxylicdianhydride. Applied Surface Science, 146396 (2020).
3. Lian X, Ma ZR, Zhang ZH, Yang JL, Sun S, Gu CD, **Liu Y**, Ding HH, Hu J, Cao X, Zhu JF, Li SZ, Chen Wei*. An in-situ spectroscopy investigation of alkali metal interaction mechanism with the imide functional group. Nano Research 13, 3224-3229 (2020).
4. Lian X, Ma ZR, Zhang ZH, Yang JL, **Liu Y**, Gu CD, Sun S, Ding HH, Hu J, Zhu JF, Li SZ*, Chen Wei*. Fluorination Guided Li Anchoring Behaviors on Phthalocyanines. J. Phys. Chem. C. 125, 8236-8243 (2021).

Multi-functionalization of a newly additive for the improved electrochemical performance of the aprotic Li-O_2 batteries

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Abstract

In order to reduce the charge overpotential of Li-O_2 batteries, many soluble additives have been explored. Among them, redox mediator (RMs) is one of the very typical representatives to ensure the good contact with the solid discharge products and to promote effective decomposition of the discharge products with lower charge overpotential. Although RMs indeed reduce the charge overpotential, the parasitic reaction between the RMs and the lithium metal anode weakens its positive role and deteriorates the total electrochemical performance of Li-O_2 batteries. In addition, most organic RMs and organometallic RMs possess large molecular size and bulky structure. However, it has been theoretically predicted that soluble catalysts with low steric hindrance can exhibit great oxidation rates. Besides, the high concentration of oxygen radical can make a solvent with high DN susceptible to nucleophilic attack, resulting in the degradation of the solvent. The solvation of oxygen radical can also diffuse to lithium metal and corrode the lithium anode, leading to the continuous degradation of electrolyte. In this report, the newly additive can not only efficiently avoid those instinct problems aforementioned based on its special structure, ultimately promoting the electrochemical performance of Li-O_2 batteries.

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Phosphorene Directed Growth of 1D NiS Nanowire Arrays for Oxygen Evolution Reaction

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Abstract

1D transition metal sulfides (TMDs) nanowires have been explored for energy-related applications due to their unique features including high surface-to-volume ratios, 1D electronic pathways for efficient charge transport, and fast strain relaxation during electrochemically driven volume expansion/contraction. However, the building-ups of TMDs nanowire arrays based on 2D sacrificing template has rarely been reported. Herein, the electrochemical exfoliated black phosphorus is utilized as the sacrificing template to produce the NiS nanowire arrays (NWAs) *via* one hydrothermal reaction. Specifically, the synthesis process and growth mechanism of NiS nanowires are discussed in detail. When used as the electrocatalysts, the NiS with improved surface exposure exhibits superior oxygen evolution reaction (OER) performance, delivering a low overpotential of only 240 mV at a current density of 10 mA cm^{-2} that outperforms the commercial RuO_2 benchmark (367 mV). The method developed for the synthesis of 1D TMSs thus provides new insights into the future development of other 1D nanowire arrays materials.

Publication List

1. **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.
2. Zhao J, Li Q, Shang T, **Wang F**, Zhang J, Geng C, Wu Z, Deng Y, Zhang W, Tao Y, Yang, Q.-H., Porous MXene monoliths with locally laminated structure for enhanced pseudo-capacitance and fast sodium-ion storage. Nano Energy 86, 106091

Pt-Ni dual atom catalyst with mass activity 21-fold higher than commercial Pt/C towards efficient hydrogen evolution

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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.[1-4] Dual-atom catalysts (DACs) with neighboring heteroatoms are expected to exert synergistic effect of the two atoms, improving the activity. Herein, we report a PtNi-NC catalyst consisting of PtNi dual-atom anchored on nitrogen-doped carbon substrate synthesized with atomic layer deposition (ALD). Characterization confirms the existence of the PtNi dual atoms. The as-prepared PtNi-NC catalyst exhibits extraordinary catalytic activity, with the overpotential of 30 mV for hydrogen evolution reaction (HER) in acidic media at a current density of 10 mA cm^{-2}, comparable to that of commercial 20 wt% Pt/C. Of particular note, PtNi-NC possesses much higher mass activity, about 21 times, than that of 20 wt% Pt/C. Density functional theory (DFT) calculations reveal that Pt-Ni dual atom generates synergistic effect by modulating the local electronic structure of Pt and Ni. This work provides the avenue for the fabrication of DACs, revealing the potential of them applied in the field of electrocatalytic HER.

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2. **Da, Y. M.**; Tian, Z. L.; Jiang, R.; Liu, Y.; Lian, X.; Shi, Y.; Wang. Y. P.; Lu, H. T.; Cui, B. H.; Zhang, J. F.; Han, X. P.; Chen, W.; Hu, W. B. Pt-Ni dual atom catalyst with mass activity 21-fold higher than commercial Pt/C towards efficient hydrogen evolution. (Summitted)
3. **Da, Y.M.**, Chen, W., The Electrochemical Society Best Poster Award, the 2nd Singapore ECS International Symposium on Energy Materials, Singapore, 20-21 November, 2021.
4. Jiang, R.; **Da, Y. M.**; Chen, Z. L.; Cui, X. Y.; Han, X. P.; Ke, H. B.; Liu, Y. H.; Chen, Y. N.; Deng Y. D.; Hu, W. B. Progress and perspective of metallic glasses for energy conversion and storage. Adv. Energy Mater., DOI: 10.1002/aenm.202101092
5. Jiang, R.; **Da, Y. M.**; Han, X. P.; Chen, Y. N.; Deng Y. D.; Hu, W. B. Ultrafast Synthesis for Functional Nanomaterials. Cell Rep. Phy. Sci. 2021, 2, 100302.

Two-Dimensional Reconfigurable Electronics Enabled by Asymmetric Floating Gate

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Abstract

Reconfigurable devices with customized functionalities hold great potential in addressing the scaling limits of silicon-based field-effect transistors. The conventional reconfigurable field-effect transistors are limited to the applications in logic circuits, and the commonly used multi-gate programming strategies often lead to high power consumption and device complexity. Here, we report a reconfigurable WSe_2 optoelectronic device that can function as photodiode, artificial synapse, and 2-bit memory in a single device, enabled by an asymmetric floating gate (AFG) that can continuously program the device into different homojunction modes. The lateral p−n homojunction formed in the AFG device exhibits high-performance self-powered photodetection, with a responsivity over 0.17 A W^{-1} and a wide detection spectral range from violet to near-infrared region. The AFG device can also mimic synaptic features of biological synapses and achieve distinct potentiation/depression behaviors under the modulation of both drain-source bias and light illumination. Moreover, when working as a 2-bit memory via the transition between n−n^+ and p−n homojunctions, the AFG device shows four distinct conductive states with a high on/off current ratio over 10^6 and good repeatability. Combining reduced processing complexity and reconfigurable functionalities, the WSe_2 AFG devices demonstrate great potential towards high-performance photoelectric interconnected circuits.

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2. **Jin, T.**; Zheng, Y.; Gao, J.; Wang, Y.; Li, E.; Chen, H.; Pan, X.; Lin, M.; Chen, W. *ACS Appl. Mater. Interfaces* ***2021,*** *13, 10639-10649.*
3. Zhang, Q.#; **Jin, T.#**; Ye, X.; Geng D.; Chen, W., Hu, W. *Adv. Funct. Mater.* ***2021,*** *31, 2106151*
4. **Jin, T.**; Gao, J.; Wang, Y.; Chen, W. *Sci. China Mater.* ***2021,*** *under review*
5. Pan, X.; **Jin, T.**; Gao, J.; Han, C.; Shi, Y.; Chen, W. *Small* ***2020,*** *16, e2001504.*
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9. Gao, J.; Lian, X.; Chen, Z.; Shi, S.; Li, E.; Wang, Y.; **Jin, T.**; Chen, H.; Liu, L.; Chen, J.; Zhu, Y.; Chen, W. *Adv. Funct. Mater,* ***2021,*** *accepted*

Construct a high-performance Li-S battery by tuning the coordination environment of Co catalyst

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Abstract

Lithium-sulfur battery (Li-S battery) possesses ultra-high energy density (2600 Wh/kg) and low cost and has been considered as a promising next generation energy storage system. However, the insulation of sulfur and discharge products (Li_2S_2 and Li_2S), as well as the large volume expansion during the cycle, hinder the practical application of Li-S battery. In addition, the shuttle effect, caused by the undesired migration of soluble polysulfide (LiPS) intermediate between the cathode and the anode, results in the low coulombic efficiency and poor cycle performance. Recently, catalysts have been employed to effectively inhibit the shuttle effect by accelerating the conversion of soluble LiPS. Rational design and development of new catalysts with higher activity are the main challenges. Herein, we synthesis a series of Co catalysts by tuning the calcine temperature. These catalysts are used as interlayer in Li-S battery. The rate and cycle performance of the battery get increased with these catalysts. The batteries still exist a capacity at around 800 mAh/g under 5 C and exist an ultralow capacity decay of 0.05% per cycle. Furthermore, the performance of Li_2S deposition test and symmetrical battery prove the catalytic ability of Co catalysts.

Publication List

1. **Yang H.T.**, Chen Wei*, Yang Quan-hong*. 2021 The Electrochemical Society Best Poster Award, the 2nd Singapore ECS International Symposium on Energy Materials, Singapore, 20-21 November, 2021

Dual Atom Catalyst for Oxygen Reduction Activity in Zinc-Air Batteries

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Abstract

Electrochemical oxygen reduction reaction (ORR) at the cathode compartment is the bottleneck in the realization of several renewable energy conversion technologies such as fuel cell, biofuel cell, and metal–air battery. To maintain the sustainable, smart, and green future, tremendous attention was immersed in the development of an economical and highly active catalyst. Rechargeable aqueous Zn-air batteries (ZABs) are considered as very promising energy storage systems because of high theoretical energy density (1084 Wh kg−1), large specific capacity, cost effectiveness, and environmental-friendly and safe operation among other energy storage devices. However, sluggish ORR kinetics associated with the cathodic compartment and high material costs are the main obstacles for the realization of its practical use in commercial sector. We prepare a highly active electrocatalyst based on dual transition metal (Co and Mn) with N-doped porous carbon. the $E_{1/2}$ of the catalyst achieved was 0.88 V in alkaline medium for ORR.

Publication List

None

Modification of the Interface between Lithium Anode and Garnet Electrolyte

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Abstract

Garnet electrolyte is a kind of promising solid state of electrolyte for the realization of lithium metal batteries due to its high ionic conductivity (10^{-4}-10^{-3} S cm^{-1}), stability against lithium metal, high modulus and the nature of nonflammable. However, the poor anodic interfacial contact severely hinder the practical application of garnet electrolyte. Recently, it was found that Li_2CO_3 could formed on the surface of garnet when exposed to the air, which leads to the limited affinity between Li metal and garnet. Here, Li_2CO_3 was removed by polishing and acid treatment, respectively. The interfacial resistance was decreased from ~1000 Ω cm^2 to ~80Ω cm^2 and ~5 Ω cm^2, respectively. Meanwhile, the lithium symmetric cells also performed stable cycling performance after the removal of Li_2CO_3 at 0.1 mA cm^{-2} and 0.2 mA cm^{-2} compared with the untreated garnet. The preliminary results showed that removing Li_2CO_3 is an effective method to improve the anodic interfacial contact.

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Tailoring Li_2O_2 Growth Route by Crystal Facet Engineering in Bifunctional Photo-assisted $Li-O_2$ Battery

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Abstract

Rechargeable lithium-oxygen batteries are expected to be a possible solution for the development of alternative batteries with high energy density. Nevertheless, the lithium-oxygen batteries are still in the prototype stage due to obstacles that are mainly related to the slow electrode dynamics, especially the high charge overpotential. To overcome these bottlenecks, the introduction of photo assistance into the lithium-oxygen system has attracted great research interest. The photo-assisted $Li-O_2$ battery is beneficial to reduce the overpotential during the charging process and significantly improve energy efficiency. However, the incomplete decomposition and accumulation of the discharge product (Li_2O_2) during the long cycles still limits the stability of the battery. Understanding and controlling the growth of the vital Li_2O_2 product is essential to overcome this challenge. Here, we propose that the crystal plane ratio of cathode catalysts could be used to tailoring the formation routes of Li_2O_2. In this work, WO_3 with different crystal plane ratios were adopted as photocathode catalysts. The (020) dominated WO_3 induced the formation of the discharge product into large spherical following the solution growth mode, while (002) dominated WO_3 catalyzed the formation of Li_2O_2 thin films through the surface growth mode. Accordingly, the performance of the battery can be tuned by regulating the crystal plane ratio, giving an ultralow overpotential of 0.07 V between the charge and discharge.

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Defect-rich Nanocatalysts fabricated by Thermal Shock for the Hydrogen Evolution Reaction

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Abstract

High-temperature thermal shock (HTS) is a rapid, low-cost, universal, and scalable way to fabricate various nanomaterials. This innovative technique is featured with instantaneously reaching an ultrahigh level (>3000 K) with the heating/cooling rate of 10^5 K s^{-1} within several milliseconds by electrical Joule heating. Defects, such as dislocation and vacancies, can be easily introduced during this near-instantaneous process and serve as active centers for catalytic reactions. Hydrogen production via water electrolysis is promising upon the development of high-performance electrocatalysts. Dislocation-rich Pt- and Ir-based nanocrystals have been proved to deliver a superior catalytic activity and stability to dislocation-deficient ones. However, the high cost and scarcity restrict the wide application of Pt-group catalysts in the large-scale production of H_2 from water electrolysis. Herein, we synthesized transition metal alloy RuNi nanoparticles on carbon black via thermal shock as a low-cost but efficient alternate for HER. The as-prepared catalyst displays a low overpotential of 27 mV at 10 mA cm^{-2} and good stability up to 20 h in the alkaline media.

Publication List

None

Silly putty-like materials for flexible/wearable electronics

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Abstract

Soft materials capable of seamlessly interfacing with living matter are highly expected to facilitate the development of flexible and even wearable electronics. Inspired by the silly putty we played in our childhood, such functional materials with similar properties of reconfigurability, stretchability, and recyclability could be designed for wide-range applications. To endow the material with smart functionality, taking conductivity as an example, conductive fillers like graphene, carbon nanotube, conductive polymers are frequently utilized. The obtained materials have been already explored for mechanical sensing, thermal sensing, and energy harvesting in the cutting-edge field of flexible/wearable electronics. However, all developed conductive silly putty-like materials are opaque, which prevents their application in optical-related flexible electronics. Based on the above literature review, we have developed a stable transparent conductive silly putty-like material for next-generation conformable devices.

Publication List

None

Fabrication of Single-atom Catalyst for Organic Coupling Reactions

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Abstract

Organic cross-coupling reactions are very essential in organic synthesis and the pharmaceutical industry. At present, the catalysts often used in cross-coupling reactions are homogeneous organic complexes. Since the homogeneous catalyst and the reaction substrate are in the same reaction phase, it is difficult to separate the catalyst and the product after the reaction effectively. In addition, the metal ions in the homogeneous catalyst will get incorporated into the final product, leading to catalyst loss and product devaluation. Therefore, developing heterogeneous catalysts for cross-coupling reactions is very attractive. Moreover, the most used palladium-based catalysts in the cross-coupling reaction are limited to large-scale production due to their high price. Therefore, the single-atom palladium catalyst is very promising among heterogeneous catalysts because of its high metal utilization and low cost. In this work, a single-atom catalyst for the Suzuki coupling reaction is reported. This catalyst is demonstrated to have high activity for the Suzuki reaction (TOF: 15000 h^{-1}, TON: 20000000), with a yield of over 90% when applied to a variety of substrates and can be used for the flow synthesis of complex natural products and drugs.

Publication List

None

Evolution of low-dimensional Phosphorus allotropes on Ag(111)

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Abstract

Phosphorus is an important non-metal element with many allotropes and tunable electronic properties. For example, as one of the most important allotropes of phosphorus, two dimensional (2D) black phosphorus (BP) possesses many extraordinary properties, such as high charge carrier mobility with high on/off ratio, thickness-dependent direct bandgap varying from 0.3 to 2 eV, and anisotropic electrical, optical and thermal properties. Inspiring by the success of 2D BP, other phosphorus allotropes with intriguing properties for next-generation electronic and optoelectronic devices have also attracted much attention. However, the transformation between different allotropes and the formation of 2D phosphorus materials are still unclear. In this work, we fully explored the emergence of different low-dimensional phosphorus allotropes on Ag(111) . New allotropes have been found and the evolution of these allotropes phase has been investigated systematically.

Publication List

Wang Y, Sun S, Zhang J, Huang Y, Chen W. *SmartMat,* 2021, 2(3): 286-298.

9th Jan 2022: NUS-TJU PhD Workshop				
Centre 3: Catalysis				
Symposium Chair: An Huan & Chang Jinquan				
		Presenter	**Title**	**Supervisors**
Morning	9:00-9:20	Shi Xiangcheng	Genetic Algorithm for Global Structure Optimization of Catalytic Surface System	Gong Jinlong & Wu Jie
	9:20-9:40	Wang Wei	Redox Catalysts Design for Chemical Looping Oxidative Dehydrogenation of Propane	Gong Jinlong & Chen Wei
	9:40-10:00	Han Xiaoyu	Cu-based catalyst for selective hydrogenation of CO2 to methanol	Ma Xinbin & Sibudjing Kawi
	10:00-10:20	Wu Zhongjie	Natural gas storage via monolithic flexible MOFs	Ma Xinbin & Zhao Dan
	10:20-10:40	Zheng Ying	Enhancing catalytic activity of Rh/CeO2 on heterogeneous hydroformylation of propylene via modifying the structure of Rh single atoms	Ma Xinbin & Yan Ning
	10:40-11:00: Break			
	11:00-11:20	Li Haoyue	Amination of alcohols using NH3 over Ir/TiO2 catalyst	Yan Ning
	11:20-11:40	Wang Sikai	Critical role of hydrogen spillover in methane activation over Mo-based polyoxometalate at room temperature	Yan Ning
	11:40-12:00	Wong Sie Shing	Quantum Yield Enhancement in Photocatalytic HCOOH Decomposition to H2 under Periodic Illumination	Yan Ning
Luch Breaak				
Centre 3: Catalysis				
Symposium Chair: An Huan & Chang Jinquan				
		Presenter	**Title**	**Supervisors**
Afternoon	14:00-14:20	Liu Rui	Numerical analysis of multi-phase reactive flow in chemical looping methane conversion	Gong Jinlong & Yan Ning
	14:20-14:40	Wei Pingping	Propane Dehydrogenation over Sulfur-doped Catalysts	Gong Jinlong & Yan Ning
	14:40-15:00	Chang Jinquan	Pd1/CsSMA Single Atom Catalyst for Electro-assisted Room Temperature Water Gas Shift Reaction	Ma Xinbin & Yan Ning
	15:00-15:20	Chen Jiyi	Surface and crystal facet-dependent effect of Pd/h-In2O3 catalyst for CO2 to methanol	Ma Xinbin & Sibudjing Kawi
	15:20-15:40	Zhou Zhaoyu	Photocatalytic Carboxylation via Carbon Dioxide Radical Anion	Ma Xinbin & WU Jie
	15:40-16:00: Break			
	16:00-16:20	An Hua	Proton-coupled electron transfer (PCET) process in heterogeneous catalytic hydrogenation	Yan Ning
	16:20-16:40	Xiao Yiying	Electrochemical reductive amination of biomass-derived feedstocks to amino acids	Yan Ning

Genetic Algorithm for Global Structure Optimization of Catalytic Surface System

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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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2. Cao, H.; Kuang, Y.; Shi, X.; Wong, K. L.; Tan, B. B.; Kwan, J. M. C.; Liu, X.; Wu, J., Photoinduced site-selective alkenylation of alkanes and aldehydes with aryl alkenes. Nat. Commun. 2020, 11, 1956.
3. Yan, J.; Cheo, H. W.; Teo, W. K.; Shi, X.; Wu, H.; Idres, S. B.; Deng, L.-W.; Wu, J., A radical smiles rearrangement promoted by neutral eosin Y as a direct hydrogen atom transfer photocatalyst. J. Am. Chem. Soc. 2020, 142(26), 11357-11362.
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Redox Catalysts Design for Chemical Looping Oxidative Dehydrogenation of Propane

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Abstract

Propene is and will remain the essential pillar of chemical and petrochemical industry because it is a 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, 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

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Cu-based catalyst for selective hydrogenation of CO_2 to methanol

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Abstract

The development of a highly efficient catalyst for CO_2 activation and selective conversion to methanol is critical to address the issues associated with the high thermal stability of CO_2 and controllable synthesis of methanol. Cu-based catalysts have been widely studied because of the low cost and excellent performance in mild conditions. However, the improvement of catalytic activity and selectivity remains challenging. Herein, we prepared hollow Cu@ZrO_2 catalysts through pyrolysis of Cu-loaded Zr-MOF for CO_2 hydrogenation to methanol. Low-temperature pyrolysis generated highly dispersed Cu nanoparticles with balanced Cu^0/Cu^+ sites, larger amounts of surface basic sites and abundant Cu-ZrO_x interface in the hollow structure, contributing to enhanced catalytic capacity for adsorption/activation of CO_2 and selective hydrogenation to methanol. In situ Fourier transform infrared spectroscopy reveals the methanol formation followed the formate-intermediated pathway. This work would provide a guideline for the design of high-performance catalysts and the understanding of the mechanism and active sites for CO_2 hydrogenation to methanol.

Publication List

None

Natural gas storage via monolithic flexible MOFs

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Abstract

Given its abundance and clean combustion, natural gas (NG) is one of the leading sources of energy to meet present demands. However, the storage and transportation of NG remain challenging. Besides the commonly used NG storage methods such as compression and liquefaction, adsorbed NG (ANG) is an attractive alternative. Despite top-performing adsorbents and present-day engineering solutions, there remain obstacles that prevent vehicles fuelled by ANG from becoming commonplace. While flexible MOFs are promising for methane storage, their expansion and shrinkage during methane sorption present problems in practical applications. To avoid MOF disintegration, the free expansion and shrinkage of the pellets should be facilitated by the vehicle's ANG system. In this vein, palletization with suitable binders may provide a feasible solution.

Publication List

1. **Wu, Z. J.**; Wee, V.; Ma, X. B.; Zhao, D., Adsorbed natural gas storage for onboard applications. *Adv. Sustainable Syst*. **2021**, 5, 2000200.

Enhancing catalytic activity of Rh/CeO_2 on heterogeneous hydroformylation of propylene via modifying the structure of Rh single atoms

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Abstract

Supported single atom catalysts (SACs) exhibit distinct catalytic activity and selectivity compared to metal clusters in many reactions. Realizing the uniformity and local environment of atomically sipersed metal atoms play significant roles for its remarkable activity and selectivity. We achieve the manipulation of local environment of SACs by changing the calcination temperature of 0.06% Rh/CeO_2 catalyst. Catalyst calcined at high temperature have more oxygen vacancies on CeO_2 which created Rh active sites with higher electron density compared with catalysts calcined at lower temperatures. This kind of Rh active sites can quikly achieve the change of valance state during hydroformylation, thus showed improved activity.

XAS and HAADF results indicated the singly dispersion of Rh on CeO_2. CO-FTIR and XPS show the increased electron density of Rh induced by high temperature calcination, which leads to stronger interaction between CO and $Rh^{\delta+}$, thus facilitating the activation of CO. in-situ FTIR results indicate that there is a faster transformation of Rh^{3+} to $Rh^{\delta+}$ during hydroformylation of propylene on high temperature calcined catalyst compared with that of low temperature calcined catalyst, accounting for the enhanced catalytic activity.

This work not only identified an efficient catalyst for hydroformylation with significantly high activity, but also benefits to the understanding of the suitable structure of single-atom catalysts that benefited to the reaction process.

Publication List

None

Amination of alcohols using NH_3 over Ir/TiO_2 catalyst

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Abstract

Alkylamines and their derivatives are extensively used in industries, and alcohols are the mainstream substrates in the alkylamines synthesis process. Iridium affords particularly low activation energy of dehydrogenation of alcohols which points out the high potential of Ir-based heterogeneous catalyst in the amination process. Here, a series of heterogeneous Ir-based catalysts with different metal oxides as supports were tested for the amination of isopropanol using ammonia in the fixed-bed reactor. The Ir/TiO_2 was identified as the best amination catalyst, affording the highest yield of 44.0 % to isopropylamine at 250 ℃. The reaction was identified to follow the dehydrogenation-condensation-hydrogenation pathway, where the dehydrogenation was verified as the rate-limiting step. The reaction kinetics, the main reactive species, the role of ammonia, and the effects of supports were investigated based on stepwise control experiments, in-situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), and X-ray spectroscopy (XPS). The catalytic activity of Ir/TiO_2 was stable enough within 20 hours at 200 ℃, and several alcohols were able to be converted to the corresponding amines.

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Critical role of hydrogen spillover in methane activation over Mo-based polyoxometalate at room temperature

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Abstract

Partial oxidation of methane under mild conditions is regarded as a dream reaction for efficient methane utilization to directly produce value-added oxygenated chemicals like methanol. However, because of the inert structure of methane, the reaction suffers from low conversion and overoxidation. Although H_2O_2 has been extensively used as the oxidant with high reactivity to produce radicals for methane activation, it is expensive and can decompose easily during the reaction, making the process far from practical.

Hydrogen spillover, a process where H atoms transfer from metal sites onto the support and often reduce the support, is closely related to many catalytic processes. Herein, we propose that H spillover on single atom Pd-supported caesium phosphomolybdate (CsPMA) is critical for partial methane oxidation with O_2 to produce methanol at room temperature. The methanol selectivity over Pd_1/CsPMA reaches to 100% with a specific activity of 12.39 mmol g_{Pd}^{-1} h^{-1} under the optimized condition with H_2 and O_2 within 30 min. Different from previous research in which in situ generated H_2O_2 is the active intermediate for the reaction, in this system, H spillover is the major reason to induce the creation of active sites for facile methane activation. Mechanistic studies suggest that atomically dispersed Pd contributes to rapid hydrogen activation and spillover to reduce POM, while methane activation and selective conversion occur on the partially reduced POM.

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Quantum Yield Enhancement in Photocatalytic HCOOH Decomposition to H_2 under Periodic Illumination

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Abstract

Controlled periodic illumination has received significant attention as a promising approach to improve the quantum yield of photocatalytic processes. Despite numerous studies on the topic, debates still exist on the dominating reason for the observed enhancements in various photodecomposition reactions. Here, we studied the effects of periodic illumination on HCOOH dehydrogenation over TiO_2-supported noble metal photocatalysts. We demonstrated that intermittent illumination at moderate frequency of approximately 7 Hz and 10% duty cycle improved the quantum yield of H_2 production by more than 2-fold, invariant of the type of metal nanoparticles deposited on TiO_2. In combination with photoelectrochemical characterisation techniques, we suggest that the promotion mechanism in periodic illumination involves enhancement in the electron charge transfer kinetics leading to more efficient electron migration to the metal nanoparticles. Kinetic isotope effect (KIE) studies suggest that Pt−H cleavage to be a rate-limiting step for H_2 productivity under both continuous and periodic illumination.

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Numerical analysis of multi-phase reactive flow in chemical looping methane conversion

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Abstract

Recently, the relative abundance of natural gas compared to other fossil fuels has led to renewed interest in selectively converting methane to value-added products via syngas. Compared with the traditional methane conversion methods, chemical looping partial oxidation of methane (CLPOM) has the advantages of low energy consumption, no air separation process and relatively high safety, attracting more attentions. Catalyst structure design and reaction mechanism study on surface reaction and lattice oxygen diffusion have been extensively explored. On the other hand, fundamental knowledge of multiphase reactive fluid dynamic behavior of the gas–solid flow needs to be clarified urgently to promote the large-scale practice of chemical looping reforming. Computational fluid dynamics (CFD) can gain insights into the interactions between chemical kinetics and fluid mechanics in chemical looping systems, but the Discrete Element Method (DEM) as the most widely used approach is limited up only to 106-108 particles, which are minuscule compared to 109-1013 particles in the industrial process.

In this work, the coarse-grained particle (CGP) approach is employed with optimized model parameters to avoid track a large number of particles by lumping many particles into a parcel. Noteworthy. high calculation accuracy and efficiency are both obtained to overcome the huge computational cost of DEM model. After lumping particles together, the collision frequency is reduced, which directly influences the energy dissipation. We first evaluate satisfying model parameters related to collision process in CGP model by resolving momentum conservation equation while the CFD results are further validated through comparing with DEM results. The lower normalized root-mean-square deviation of pressure drop distribution in axial direction together with solid fraction and vertical velocity distribution in radial direction indicate the high accuracy of CGP model with optimized parameters by employing a lower statistic weight. This reactive multiphase CFD model with CGP means is then developed and implemented using a Fortran code to simulate the reduction step in chemical looping methane combustion over NiO catalyst. Especially, the solid conversion and products distribution both have good agreements with experimental and DEM results, respectively, indicating the high accuracy of CGP model. The influence of catalyst inventory and methane partial pressure on catalytic performance are explored systematically. As the decrease of catalyst inventory to increase the weight space velocity, the solid conversion and products yield are enhanced first and then keep constant after eliminating the external diffusion, while the solid conversion always has a positive relation with methane concentration. Hence, the fast and reliable coarse gain particle model enable us to tackle more practical large-scale CLPOM reaction systems.

Publication List

None

Propane Dehydrogenation over Sulfur-doped Catalysts

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Abstract

Propylene (C_3H_6) is one of the most significant raw materials in petrochemical industry. The direct dehydrogenation of propane to propylene (PDH) has been considered as a promising method to yield propene "on purpose". Pt-based catalysts are effective in PDH due to the affinity of Pt for paraffinic C–H bonds. Nevertheless, Pt catalysts are vulnerable to deactivation owing to coking and Pt sintering under high temperatures. Previously, it has been proved that engineered metal oxides such as TiO_2 modified Al_2O_3 alleviated coke deposition and metal sintering in PDH. In this work, we synthesized Pt catalysts supported on sulfur-doped TiO_2–Al_2O_3 binary oxide to further improve the catalyst. The sulfur was successfully doped in the lattice of TiO_2. The aim of our study was to investigate how does sulfur doping affects the Pt-support interaction and its consequence on PDH activity as well as catalyst stability.

Publication list:

None

Pd_1/CsSMA Single Atom Catalyst for Electro-assisted Room Temperature Water Gas Shift Reaction

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Abstract

The water-gas shift (WGS) reaction is an important reaction in industry for the elimination of carbon monoxide (CO) to produce high-purity hydrogen (H_2); however, this process operates at high temperature and requires gas separation of H_2 from methane (CH_4), carbon dioxide (CO_2) and residual CO, resulting in energy loss. Designing electrochemical redox paths to decouple CO oxidation and H_2 production at the anode and cathode, respectively, provides an alternative strategy to avoid H_2 separation. Herein, we report a low overpotential WGS process using a polyoxometalate-based palladium single-atom catalyst (Pd_1/CsSMA) in phosphomolybdic acid (PMA) aqueous solution at room temperature. The Pd_1/CsSMA and PMA solution, acting as redox mediators and buffers, respectively, connects thermal catalysis of CO oxidation with electrocatalysis of H_2 evolution. The reduction degree of PMA solution is critical to the performance of the catalyst. After optimization, the catalyst shows excellent turnover frequency (1.2 s^{-1}) and high durability (10 h). This process provides a promising route for producing high-purity H_2 via electro-assisted WGS under mild condition.

Publication List

None

Surface and crystal facet-dependent effect of Pd/h-In2O3 catalyst for CO2 to methanol

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Abstract

Developing thermal catalysts to exploit the abundant carbon source in CO_2 is deemed to be an essential part of the alleviation of environmental issues caused by CO_2 over-emission. Attracted by the fascinating prospects of “methanol economy”, CO_2 hydrogenation to methanol is among the most promising applications of CO_2 catalysis. Cu-based catalyst Cu-ZnO-Al_2O_3 is the most common catalyst in industrial commercialized methanol synthesis since it was proposed. However, the catalytic performance of Cu-ZnO-Al_2O_3 is still unsatisfactory due to the deactivation phenomenon and poor methanol selectivity. Recently, indium oxide (In_2O_3) has been popular in research since it was found to have huge potential to serve as a candidate thermal catalyst for industrial CO_2 hydrogenation to methanol in theoretical and experimental ways.

Herein, a new indium-based catalyst, Pd/h-In_2O_3, for catalytic CO_2 hydrogenation to methanol was designed by integrating crystal phase control with supported catalysts. Thanks to the promotion effects of Palladium (Pd) species on accelerating the kinetics of hydrogen dissociation, as well as the stronger affinity for methanol synthesis intermediates of some specific crystal planes of h-In_2O_3, Pd/h-In_2O_3 displays a good catalytic performance with high CO_2 conversion and methanol selectivity.

Publication List

None

Photocatalytic Carboxylation via Carbon Dioxide Radical Anion

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Abstract

Photosynthesis plays a crucial role for life by absorbing carbon dioxide and generating both oxygen and biomass. Chemists have long been mimicking the magic of plants and attempted to utilize light in chemistry. Meanwhile, to achieve carboxylation reaction, carbon dioxide, a well-known greenhouse gas which widely exists in the atmosphere, is an ideal C1 source in organic synthesis. During the organic reaction, the generation of carbon dioxide radical anion can be a potent intermediate to react with other substrates, however, it's generally hard to produce carbon dioxide radical anion given its redox potential. Herein, I'm trying to utilize light to generate carbon dioxide radical anion and perform the carboxylation reaction.

Publication List

None

Proton-coupled electron transfer (PCET) process in heterogeneous catalytic hydrogenation

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Abstract

Proton-coupled electron transfer (PCET) process is ubiquitous in chemistry and biology to describe reactions and half reactions in which both electrons and protons are transferred. On the other hand, thermochemical hydrogenation over heterogeneous catalysts, one of the most important reactions in industry for making fuels, organic chemicals and ammonia, is often believed to occur via hydrogen atom transfer to the target molecules. Herein, we test the hypothesis that thermochemical hydrogenation can proceed via two coupled electrochemical half-reactions including hydrogen oxidation and substrates reduction respectively. Noble metal catalysts (Pt, Pd and Rh) promoted hydrogenation of nitro group-, C-C double bond- and C-C triple bond-containing substrates are comparatively tested in H-type electrolytic cell (H-cell) and single electrolytic cell (S-cell). In H-cell, H_2 and substrates are independently supplied into two chambers which are separated by proton exchange membrane, while in S-cell all reactants are supplied into the same chamber. Indeed, the activity and selectivity collected in H-cell are well matched with that in S-cell over a broad range of substrates, catalysts and reactions conditions, indicating that the reaction mechanism of electrochemical and thermochemical hydrogenation has same/similar origin. Reaction kinetics test, electron-capture experiment and isotopic experiment further suggest that the electrochemical pathway is important and even dominant for liquid-phase hydrogenation reactions. These findings provide a new angle to view thermal catalytic hydrogenation; hydrogen acts as an electron and proton donor, while the reduction of substrates provides an electrochemical driving force. This research hints that thermochemical and electrochemical hydrogenation reactions are fundamentally connected, thereby enabling the rational design of thermal hydrogenation catalysts applying knowledge gained in electrochemical processes.

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Electrochemical reductive amination of biomass-derived feedstocks to amino acids

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Abstract

As the building blocks of life, amino acids are widely used as precursors to make food additives, pharmaceutical products and bio-polymer. Currently, amino acids synthesis mainly relies on microbial culturing processes which require long fermentation time and troublesome purification steps. In contrast, chemical methods including thermocatalytic and photocatalytic transformation of renewable feedstocks and abundant NH3 into amino acids are highly desirable. Apart from these strategies, electrochemical reductive amination offers a potentially efficient pathway to organonitrogen chemicals by using renewable electricity as reductant and water as proton source under benign reaction conditions. However, most electrodes reported so far for this reaction are based on precious Pt, Pd metals, or toxic metals such as Hg and Pb.

Here, earth-abundant metal oxides (TiO2, WO3, CeO2 and MoO3) with high selectivity towards electroreduction of imine and/or carbonyl groups and large overpotential for the competing hydrogen evolution reaction (HER) were employed for the reductive amination of biomass-derived α-ketoglutaric acid in the presence of NH3 as nitrogen source to produce glutamic acid. The yield of glutamic acid follows the order of TiO2 > MoO3 > CeO2 ≈ WO3. MoO3 and CeO2 were discovered as highly selective cathode materials towards glutamic acid synthesis with nearly 100% faradaic efficiency, while the byproduct α-hydroxyglutaric acid was obtained with TiO2 and WO3. High catalytic performance was likely attributed to the formation of oxygen vacancies and to the interconversion of different metallic oxidation states during the application of electrons, which are favourable for the adsorption of hydrophilic imine and carbonyl groups. The activities of transition metals (Pt, Pd, Au) immobilized on TiO2 were also investigated, while the adverse HER served as the dominating reaction.

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