3rd NUS-TJU PhD Online Workshop
7th-8th Jan 2023

天津大学–新加坡国立大学
福州联合学院

3rd 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, four research centers have been established including Emerging Optoelectronics and Flexible Electronics Center, Advanced Manufacturing Center, Energy Materials and Catalysis Center and Center for Frontier Fundamental Physics.

Following the signing of agreements on December 1st, 2018, the brand new campus is expected to be fully functional for research and education in Feb 2023. 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 third in its series taking place online in January 2023. 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.

2023 Workshop Organizing Committee (Students):
Zhang Qing, Xiong Xincheng, Song Xianneng, Lin Zhikeng, Huang Qingqin, Zeng Hao, Zhang Bihan, Lin Hongbin, Yang Zhucheng, Wang Meng, Yang Haotian, Wang Sikai, An Hua, Xu Di

2023 Workshop Organizing Committee (Pis):
Chen Wei, Xie Jianping, Yan Ning, Zhao Yu, Li Liqiang

Catalogue

Workshop Schedule

NUS-TJU PhD Online Workshop, 7th-8th Jan 2023

Center 1: Optoelectronics

Symposium Chair: Zhang Qing

		Presenter	Title	Supervisor
Session Chair: Zhang Qing				
7th Jan Morning	9:00-9:15	Chen Fangzheng	Metallo-COFs based on pyridine-bis(imine)	Loh Kian Ping
	9:15-9:30	Leng Xiaohui	Selective Conversion of Benzylamine Catalysed by Defect-rich $ZnIn_2S_4$	Loh Kian Ping
	9:30-9:45	Song Jingting	Promoting Dinuclear-Type Catalysis in Cu_1-C_3N_4 Single Atom Catalyst	Loh Kian Ping
	9:45-10:00	Li Zhuo'er	Design and Function of π Electronic Covalent organic frameworks	Jiang Donglin
	10:00-10:15	Xie Shuailei	Design and Synthesis of Novel Architectures of Covalent Organic Frameworks	Jiang Donglin
	10:15-10:30	Yang Hao	Designed Synthesis of Novel Covalent Organic Frameworks	Jiang Donglin
	10:30-10:45: Break			
	Session Chair: Zhang Qing			
	10:45-11:00	Xin Shan	The Aromaticity of expanded radialenes and its charged species	Wu Jishan
	11:00-11:15	Zhang Qiuyu	Study of Indenofluorene Macrocyclic Oligomers	Wu Jishan
	11:15-11:30	Zhou Qifeng	Facile Synthesis of a Twisted Figure-Eight Carbon Nanobelt	Wu Jishan
	11:30-11:45	Wang Congyong	Metal Halide Perovskite/Organic Semiconductor-based Field-Effect Transistors	Hu Wenping
	11:45-12:00	Zhang Qing	Ultralow-power Vertical Transistors for Multilevel Decoding Modes	Hu Wenping
	12:00-12:15	Zhu Xiaoting	High-contrast gate-tunable bidirectional synapses based on 2D molecular crystal heterojunctions for motion detection	Hu Wenping

Lunch Break				
		Presenter	Title	Supervisor
Session Chair: Zhang Qing				
7th Jan **Afternoon**	14:00-14:15	Pu Guiqiang	Organic-Inorganic Hybrid Photon Upconversion with Ultralong Kinetic Decay for Optical Encryption	Li Zhen
	14:15-14:30	Wang Zao	Activating photocatalytic hydrogen evolution by constructing Ni-based organical layers and tailoring its crystal facets	Li Zhen
	14:30-14:45	Zhao Yao	Organic Luminogens with Stimulus-responsive Room Temperature Phosphorescence	Li Zhen
	14:45-15:00	An Chuanbin	A Strategy for Improving N-type Transistor Performance or Possessing Synaptic Behavior on the Basis of Imparting Stretchability	Geng Yanhou
	15:00-15:15	He Yu	Thienoisoindigo-based Quinoids: Synthesis and Properties	Geng Yanhou
	15:15-15:30	Shao Bo	Synthesis of Thieno[3,4-b]thiophene-Based Quinoids: Effect of π–conjugated Backbone Length on Properties	Geng Yanhou
	15:30-15:45: Break			
	Session Chair: Xiong Xincheng			
	15:45-16:00	Zheng Haining	Solid-solid Crystal Conversion in Chiral Hybrid Perovskites with Paramagnetic-to-Ferromagnetic Transition	Loh Kian Ping
	16:00-16:15	Zhu Youhuan	Strain and disorder stacking-induced breaking of odd-even effect in few-layer SnS	Loh Kian Ping
	16:15-16:30	He Weixin	Two-Dimensional Ferroelectric Dion-Jacobson Perovskite	Loh Kian Ping
	16:30-16:45	Shen Tong	Fused Triangulene Dimer: Synthesis and Application for NIR Laser	Wu Jishan
	16:45-17:00	Sun Zhitao	Chiral-twisted fused dibenzo-zethrene dimer and trimer	Wu Jishan
	17:00-17:15	Zhang Boyi	A Graphyne Spoked Wheel	Wu Jishan

Workshop Schedule

NUS-TJU PhD Online Workshop, 7th-8th Jan 2023

Center 1: Optoelectronics

Symposium Chair: Xiong Xincheng

		Presenter	Title	Supervisor
Session Chair: Xiong Xincheng				
8th Jan Morning	9:00-9:15	Xiong Xincheng	Polymeric Field-effect Transistors Achieved by Solution Methods and Understanding of Morphology-Performance Relationships	Li Liqiang
	9:15-9:30	Zhang Jing	Fluorescent Lateral-Flow Immunoassays for SARS-CoV-2 Detection	Li Liqiang
	9:30-9:45	Shi Zhuojie	Multi-functional interface modifiers for high efficiency perovskite solar cell	Li Liqiang
	9:45-10:00	Cao Yalei	Organic Fluorophores with Chemiluminescence for Sensing and Imaging of Reactive Oxygen Species	Li Zhen
	10:00-10:15	Jiang Wanqing	Stable luminescent radicals applied in optoelectronic applications with doublet emission	Li Zhen
	10:15-10:30: Break			
	Session Chair: Xiong Xincheng			
	10:30-10:45	Xu Duo	Study on Stimulus-responsive Room-temperature Phosphorescent Materials	Li Zhen
	10:45-11:00	Chen Xiaofeng	Electron-Rich Ladder-Type Aromatics and Their Low Bandgap Conjugated Molecules and Polymers	Geng Yanhou
	11:00-11:15	Fan Renzhen	Convergent Synthesis of the Precursors to Thiophene-Based Quinoids	Geng Yanhou
	11:15-11:30	Shi Kaimin	Synthesis and characterization of conjugated materials based on isoindigo derivatives	Geng Yanhou

Lunch Break				
		Presenter	**Title**	**Supervisor**
Session Chair: Song Xianneng				
8th Jan Afternoon	14:00-14:15	Pan Jinhui	Thiophene-based polymer for photochemical energy conversion	Loh Kian Ping
	14:15-14:30	Wang Ming	Hybrid Copper Halide Perovskites with Ferroelectric and Ferromagnetic Property	Loh Kian Ping
	14:30-14:45	Liu Hongtian	A COF membrane based on electrospinning for ultra-fast separation of oil/water emulsion	Loh Kian Ping
	14:45-15:00	Ye Zhuolin	π-conjugated macrocycle and organic electrode materials	Wu Jishan
	15:00-15:15	Wu Chun	Thienopyrazine-based Macrocycle and Oligomer with Diradicaloids	Wu Jishan
	15:15-15:30	Jiang Jiaqi	Open-shell polymer	Wu Jishan
	15:30-15:45: Break			
	Session Chair: Song Xianneng			
	15:45-16:00	Li Pengfei	P-block metal-based nanostructure for efficient CO2 electroreduction	Li Liqiang
	16:00-16:15	Wang Liwei	Low temperature STM investigation of self-assembly and reaction of C8-BTBT	Li Liqiang
	16:15-16:30	Song Xianneng	Field-induced organic light emitting diodes driven by alternating current	Li Liqiang
	16:30-16:45	Chi Zhihe	Two-photon-excited organic room temperature phosphorescent materials	Li Zhen
	16:45-17:00	Shan Yifei	Water Induced Room Temperature Phosphorescence	Li Zhen
	17:00-17:15	Pang Pengfei	The synthesis and characterization of imide-containing ladder type building blocks	Geng Yanhou
	17:15-17:30	Bai Junhua	Unraveling the Stability-Morphology of Nonfullerene Organic Solar Cells	Geng Yanhou

Metallo-COFs based on pyridine-bis(imine)

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Abstract Text

Covalent organic frameworks (COFs) and metal-organic frameworks (MOFs) have drawn tremendous interest over the past decade, not only because of their designable and crystalline porous architectures, but also because of the fascinating properties that arise from the unique structures. Therefore, it is of great interest to combine the sophisticated functionalities of MOFs and the stability of COFs by hybridizing metal ions with covalent linkages to obtain a new kind of material metallo-COFs. So far, the development of metallo-COFs is still in its infancy, and the building blocks used to construct metallo-COFs are rare owing to the synthetic difficulty of hybridizing metal ions and covalent linkages while maintaining crystallinity. Here, we report a new building block for metallo-COFs, pyridine-bis(imine) (pdi). Based on pdi, a metallo-COF (pdiCOF-Zn-1) and its nonmetal counterpart (pdiCOF-1) were synthesized.

Publication List

None

Selective Conversion of Benzylamine Catalysed by Defect-rich ZnIn2S4

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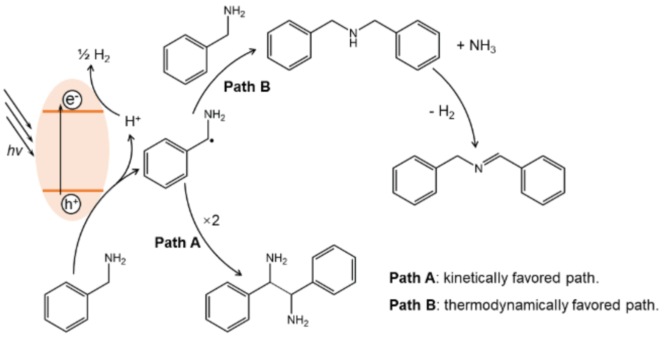
Abstract Text

Light induced oxidative coupling of organic compounds becomes an important synthetic route under mild conditions. Functional groups such as amino groups in the alkane can react with the carbon radical to block the C-C bond formation due to their high activities in a photocatalytic process. In practice, the product of selective conversion of benzylamine is usually an imine. The photocatalytic conversion of benzylamine into its C-C product with high selectivity is still rare over $ZiIn_2S_4$. Here we demonstrate the C-C bond formation of benzylamine can be reached through defect engineering of $ZnIn_2S_4$. C-C selectivity of ~80% is realized under the benzylamine conversion of ~80%. Further study reveals the wavelength-depended product conversion of benzylamine. The selective conversion of benzylamine is ascribed to the different reaction paths under different irradiation conditions.



Publication List

None

Promoting Dinuclear-Type Catalysis in Cu1-C3N4 Single Atom Catalyst

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Abstract Text

Reducing particle size in supported metal catalyst to single atom level isolates the active metal sites and maximizes the atomic utilization efficiency. However, the large inter-atom distance, particularly in low-loading single atom catalyst (SAC), is not favourable for a complex reaction where two (or more) reactants have to be activated. A key question is how to control the inter-atom distances to promote dinuclear-type co-activation at the adjacent metal sites. Here, we report that reducing the average inter-atom distance of Cu_1 SAC supported on C_3N_4 to 0.74 ± 0.13 nm allows these catalysts to exhibit dinuclear-type catalytic mechanism in nitrile-azide cycloaddition. Operando X-ray absorption fine structure study reveals a dynamic ligand exchange process between nitrile and azide, followed by their co-activation on dinuclear Cu SAC sites to form the tetrazole product. This work highlights that reducing the nearest neighbour distance of SAC allows mechanistic pathway to diversify from single site to multi-site catalysis.

Publication List

[1] **Song, J.**#; Chen, Z.#; Cai, X.#; Zhou, X.; Zhan, G.; Li, R.; Wei P.; Yan, N.; Xi, S.* and Loh, K. P.* Promoting Dinuclear-Type Catalysis in Cu_1–C_3N_4 Single-Atom Catalysts. *Adv. Mater.* **2022**, 34, 2204638.

[2] **Song, J.**; Liu, J.; Loh, K. P.; Chen, Z.* Ultrahigh Loading Copper Single Atom Catalyst for Palladium-free Wacker Oxidation. *Chem. Res. Chinese Universities*, **2022**, 38(5), 1239.

[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. *Nat. Commun.* **2022**, 13, 2807.

[4] 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.

Design and Function of π Electronic Covalent organic frameworks

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Abstract Text

Covalent organic frameworks (COFs) are a class of crystalline porous polymers that can be designed by topology diagram and synthesized via polycondensation reactions to produce organic materials with highly ordered structures. Over the past 15 years, advances in chemistry 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 pre-designability, 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 on 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 Text

Covalent organic frameworks (COFs) represent an emerging class of crystalline porous polymer that can be constructed with organic building blocks by topology-directed polymerization. Especially, COFs exhibit unique porous features and skeleton characteristics that 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 understanding of the interplays of COFs with ions and molecules.

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

Publication List

[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 sp^2-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 Text

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. 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.

Since the reversible reactions have been widely employed in the synthesis of crystalline COFs, the exploration of irreversible reaction for the synthesis of COFs with stronger bonds that endow COFs with excellent chemical and thermal stabilities further expands the scope of polymerization reactions in COFs synthesis. The preparation of COFs linked by stronger bond has become a long sought objective in synthetic chemistry. 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] Ruoyang Liu, Ke Tian Tan, Yifan Gong, Yongzhi Chen, Zhuoer Li, Shuailei Xie, Ting He, Zhen Lu, **Hao Yang**, and Donglin Jiang*. Covalent Organic Frameworks: An Ideal Platform for Designing Ordered Materials and Advanced Applications. Chem. Soc. Rev., 2021, 50, 120-242.

The Aromaticity of expanded radialenes and its charged species

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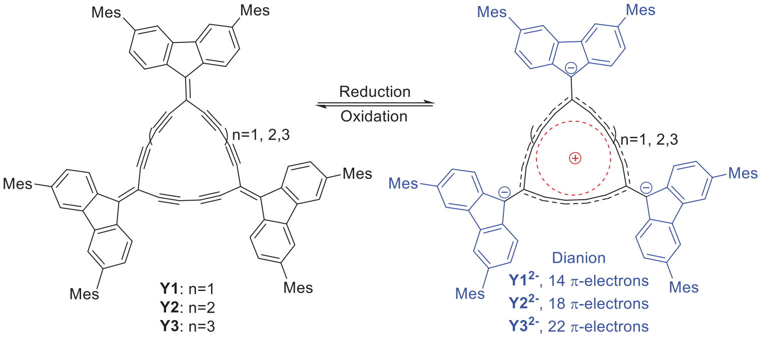
Abstract Text

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

[1] Shan Xin, Yi Han, Wei Fan, Xuhui Wang, Yong Ni, Jishan Wu. Enhanced Aromaticity and Open-Shell Diradical Character in the Dianions of 9-Fluorenylidene-Substituted Expanded Radialenes. Angew. Chem. Int. Ed. 2022, 134, e202209448

Study of Indenofluorene Macrocyclic Oligomers

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Abstract Text

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 recent research on polyradicaloids focuses on synthesising stable radical compounds. The study of fundamental concepts such as aromaticity and valence tautomerisation of the polyradicaloids systems 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 this study, 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.

Publication List

None

Facile Synthesis of a Twisted Figure-Eight Carbon Nanobelt

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Abstract Text

Twisted carbon nanobelts are attractive molecular nanocarbons of topologically unique structures, appealing properties, and potential applications, while their synthesis remains a big challenge. Here we report a facile synthesis of an unprecedented figure-eight shaped carbon nanobelt **1** through Suzuki-Miyaura coupling and subsequent Bismuth(III)-catalyzed cyclization. The scaffold of **1** can be visualized as the outcome of the fusion of two [5]helicene with two anthracene subunits. Its helically twisted structure was confirmed by X-ray analysis. The overcrowded skeleton enabled the persistent shape of **1**, thus making the enantiomers of **1** can be resolved by a chiral HPLC. The photophysical properties of **1** were well investigated by UV−vis absorption and fluorescence spectroscopic studies and density functional theory calculations. **1** shows moderate |gabs| and relatively high |glum| values according to the circular dichroism (CD) and circularly polarized luminescence (CPL) measurements.

Publication List

[1] **Zhou, Q.**; Hou, X.; Wang, J.; Ni, Y.; Fan, W.; Li, Z.; Wei, X.; Li, K.; Yuan, W.; Xu, Z.; Zhu, M.; Zhao, Y.; Sun. Z.; Wu, J. Pending for submission, **2022**.

[2] Li, Z.; Hou, X.; Han, Y.; Fan, W.; Ni, Y.; **Zhou, Q.**; Zhu, J.; Wu, S.; Huang, K.-W.; Wu, J. *Angew. Chem. Int. Ed.* **2022**, 61, e202210.

[3] Fan, W.; Matsuno, T.; Han, Y.; Wang, X.; **Zhou, Q.**; Isobe, H.; Wu, J. *J. Am. Chem. Soc.* **2021**, *143*, 15924-15929.

Metal Halide Perovskite/Organic Semiconductor-based Field-Effect Transistors

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Abstract Text

Recently, metal halide perovskite, emerging as the next generation semiconducting materials, have attracted wide attention due to their remarkable optoelectronic performances of strong light absorption, tailored band gap, long charge-carrier diffusion length, as well as narrow emission width. These excellent characteristics, along with good solution processibility and convenient synthesis, 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 metal halide perovskite will result in gate-field screening effect, which further contributes to relatively low charge mobility under room temperature. Moreover, traditional metal lead halide perovskite has the innate disadvantage of toxicity. To address these issues, we aim to design and construct diverse perovskite/organic semiconductor (polymer and organic small molecule) based FETs. 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, and optical switch.

Publication List

[1] **Wang, C. Y.**; Sun, Q. S.; Peng, G; Yan, Y. J.; Yu, X. P.; Li, E. L.; Yu, R. J.; Gao, C. S.; Zhang, X. T.; Duan, S. M.; Chen, H. P.; Wu, J. S.; Hu, W. P. $CsPbBr_3$ quantum dots/PDVT-10 conjugated polymer hybrid film based photonic synaptic transistors toward high-efficiency neuromorphic computing, *Sci. China Mater*. **2022**, *65*, 3077.

[2] **Wang, C. Y.**; Zhang, Z. C.; Zhu, Y. T; Yang, C. H.; Wu, J. S.; Hu, W. P. Two dimensional covalent organic frameworks: From synthetic strategies to advanced optical-electrical-magnetic functionalities, *Adv. Mater*. **2022**, 2102290.

[3] Li, J. J.#; **Wang, C.Y.#**; Wang, D. J.#; Yang, C. H.#; Cui, X. Y.; Gao, X. J.; Zhang, Z. C. Bi^{3+}-Based Ellagate MOF with Acid/Base Resistance Boosting Carbon Dioxide Electroreduction to Formate, *J. Mater. Chem. A*. **2022**, *10*, 20018.

[4] **Wang, C. Y.#**; Yang, C. H.#; Zhang, Z. C. Unraveling molecular-level mechanisms of reactive facet of carbon nitride single crystals photocatalyzing overall water splitting, *Rare Metals*, **2020**, *39*, 1353.

[5] Gao, Z. Q.#; **Wang, C. Y.#**; Li, J. J.; Zhu, Y. T.; Zhang, Z. C.; Hu, W. P. Conductive Metal-Organic Frameworks for Electrocatalysis： Achievements, Challenges, and Opportunities. *Acta Phys. -Chim. Sin*. **2020**, *37*, 2010025.

Ultralow-power Vertical Transistors for Multilevel Decoding Modes

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Abstract Text

Organic field-effect transistors with parallel transmission and learning functions are of interest in the development of brain-inspired neuromorphic computing. However, the poor performance and high power consumption are the two main issues limiting their practical applications. Herein, we demonstrate an ultralow-power vertical transistor based on MXene and organic single crystal. The transistor exhibits a high J_{ON} of 16.6 mA/cm^2 and a high J_{ON}/J_{OFF} ratio of 9.12×10^5 under an ultralow working voltage of -1 mV. Furthermore, it can successfully simulate the functions of biological synapse under electrical modulation along with consuming only 8.7 aJ of power per spike. It also permits multilevel information decoding modes with a significant gap between the readable time of professionals and non-professionals, producing a high signal-to-noise ratio up to 114.15 dB. This work encourages the use of vertical transistors and organic single crystal in decoding information and advances the development of low-power neuromorphic systems.

Publication List

[1] **Zhang, Q.**#; Li, E.#; Wang, Y.; Gao, C.; Wang, C.; Li, L.; Geng, D.; Chen, H.; Chen, W.; Hu, W. Ultralow-power Vertical Transistors for Multilevel Decoding Modes. *Adv. Mater.* **2022**, DOI: 10.1002/adma.202208600.

[2] **Zhang, Q.**#; Jin, T.#; Ye, X.; Geng, D.; Chen, W.; Hu, W. Organic Field Effect Transistor-Based Photonic Synapses: Materials, Devices, and Applications. *Adv. Funct. Mater.* **2021**, *31*, 2106151.

[3] **Zhang, Q.**#; Xiao, X.#; Li, L.; Geng, D.; Chen, W.; Hu, W. Additive-assisted growth of scaled and quality 2D materials. *Small* **2022**, *18*, 2107241.

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High-contrast gate-tunable bidirectional synapses based on 2D molecular crystal heterojunctions for motion detection

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Abstract Text

Bidirectional optoelectronic synapses that combine excitatory and inhibitory synapses are crucial for imitating biologic neuromorphic system, reversibly processing information and online training for artificial neuromorphic algorithms. However, there are still huge challenges for bidirectional optoelectronic synaptic devices to obtain high responsivity and contrast ratio. Herein, a bilayer 2D molecular crystal (2DMC) p-n heterojunction is developed to achieve bidirectional synaptic behavior. The 2DMC heterojunction organic field effect transistor (OFET) devices exhibit typical ambipolar property and remarkable responsivity (R) of 3.58×10^{4} A W^{-1} under weak light as low as 0.008 mW cm^{-2}. Excitatory and inhibitory synaptic behaviors are successfully realized by the same light stimuli under different gate voltage. Moreover, superior contrast ratios (CR) for both excitatory (17) and inhibitory (1.53×10^{3}) synapses are demonstrated by the ultrathin and high-quality 2DMC heterojunction, which transcends previous bidirectional optoelectronic synapses and are applied for the motion detection of the pendulum. Furthermore, a motion detection network based on the device is developed for the detection and recognition of classic motion vehicles in road traffic with the accuracy exceeding 90%. This work provides an effective strategy for developing high contrast bidirectional optical synapses and show great potential in intelligent bionic device and future artificial vision.

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Organic-Inorganic Hybrid Photon Upconversion with Ultralong Kinetic Decay for Optical Encryption

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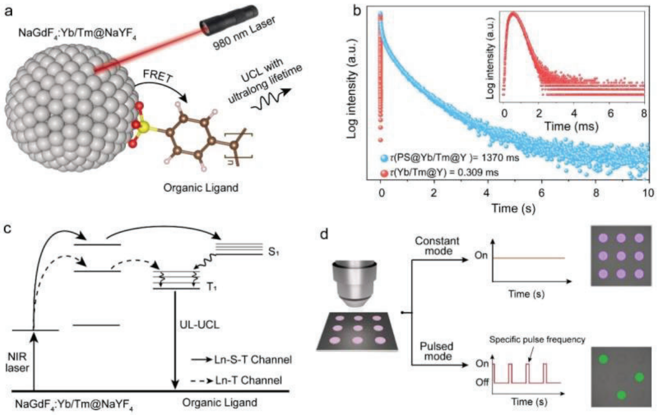
Abstract Text

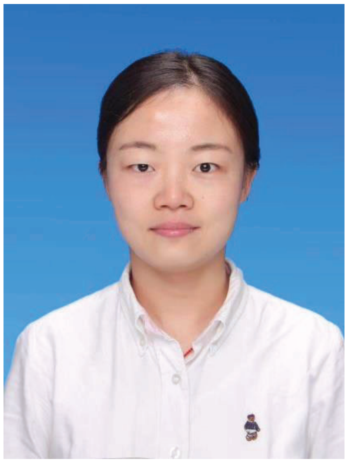
Expanding the kinetic decay of upconverted luminescence (UCL) of nanocrystals doped with lanthanides (Ln^{3+}) up to several seconds is crucial and challenging for bioimaging and optical encryption. Here, we report an organic-inorganic hybrid approach to achieve ultralong-lived UCL (UL-UCL) under ambient conditions. The UL-UCL lifetime of hybrid materials can reach 1.37s, which is about 4500-fold of the intrinsic UCL lifetime of Ln^{3+} ions. The characteristic radiation of UL-UCL is controllable by employing specific organic ligands. Two excitons migration channels involving Ln-S-T and Ln-T are investigated. Eventually, we provide a pulsed laser-pumped encryption system that provides a higher level of encryption than conventional UCL encryption strategies. This work not only provides a new strategy for realizing UL-UCL, but also presents a perspective to understand the excitonic movement between Ln3+ ions and triplet states of organic ligands.



Publication List

None

Activating photocatalytic hydrogen evolution by constructing Ni-based organical layers and tailoring its crystal facets



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Abstract Text

The development of highly active and stable cheap cocatalysts is critical for photocatalytic hydrogen evolution reaction (HER). Metal-organic frameworks have attracted much attention because of their high aspect ratio and well-defined coordination structures, but they always are catalytically inactive due to the sluggish reaction kinetics. In this work, two Ni metal-organic layers (MOLs), Ni-MOL-100 exposing rich (100) crystal facets and Ni-MOL-010 exposing (010) crystal facets have been synthesized by tuning the molar ratios of metal ions and organic ligands. Compared with the bulky structure, their catalytic activities of MOLs are activated for HER. Impressively, Ni-MOL-100 shows 12 times higher activity than that of MOL-010. Experimental and theory calculation results show that the enhanced activity of Ni-MOL-100 is attributed to its appropriate conduction band potential to promote the photo generating carriers transfer, and more explosion of coordination-unsaturated Ni(II) ions site with optimized hydrogen adsorption free energy to accelerate hydrogen evolution reaction rate. This work demonstrates the important role of crystal surface tailoring engineering in the design of photocatalytic hydrogen evolution cocatalysts.

Publication List

None

Organic Luminogens with Stimulus-responsive Room Temperature Phosphorescence

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Abstract Text

Stimulus-responsive RTP is the room temperature phosphorescence (RTP) properties that can be tuned by external stimulus, such as heating, light irradiation, water vapor, ammonia gas and so on. Achieving the organic materials with these properties is significant and attractive. Here, three triphenylamine (TPA) derivatives with a trifluoromethyl group are designed and synthesized. Then, these organic molecules are doped into polymer matrix of PS, PMMA, PVA and PVP. Outstanding RTP performance (1.84 s) is observed from these phosphors doped films. Subsequent experiments show that the luminogens with more locally excited (LE) state show a better RTP effect, while those with more charge transfer(CT) state do not. The RTP performance of these doped films change dramatically after UV light irradiation, steam fumigation and heating, because the interactions between phosphors and polymer matrix or other molecules are influenced by the stimulation. Finally, the materials are successfully applied in screen printing and information encryption.

Publication List

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A Strategy for Improving N-type Transistor Performance or Possessing Synaptic Behavior on the Basis of Imparting Stretchability

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Abstract Text

Compared with the p-type stretchable transistor, the development of n-type stretchable transistor is slow. Few n-type stretchable transistors have been reported to date, and those that have been reported possess low mobility. Here, we use PBTTT-based multiblock copolymer synthesized in previous work to physically blend with n-type material IIDSiC8 with high mobility. High mobility n-type stretchable semiconductor and n-type stretchable synaptic semiconductor can be obtained by adjusting the blending ratio. When the blending mass ratio (multiblock copolymer : IIDSiC8) is less than 1:1, the blending nanofilm shows typical n-type transistor behavior. The IIDSiC8 nanofilm showed obvious bipolar behavior in the top-gate bottom-contact device. When 5 wt% multiblock copolymer (blend ratio 20:1) was added into IIDSiC8 matrix, a small number of holes were captured by the discontinuous p-type multiblock copolymer. The blending nanofilms showed typical n-type transfer behavior and the current on/off ratio was greatly increased. Considering the mobility and mechanical properties at the same time, we finally chose the blend ratio of 3:1 with COS larger than 100% and the highest mobility of 1.71 $cm^2V^{-1}s^{-1}$. The electrical properties are almost not reduced after 1000 times of cyclic stretching under 100% strain, proving that this is a successful strategy for the preparation of high mobility n-type transistors. In addition, when the blending ratio is greater than 1:1, the transistor has typical synaptic behavior, providing the potential for the preparation of stretching n-type synaptic transistors.

Publication List

None

Thienoisoindigo-based Quinoids: Synthesis and Properties

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Abstract Text

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 as the building block substituted with indadione termini will be studied and prepared OFETs to explore the effect of alkyl chain length on charge transport properties.

Publication List

None

Synthesis of Thieno[3,4-b]thiophene-Based Quinoids: Effect of π–conjugated Backbone Length on Properties

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Abstract Text

Quinoidal oligothiophenes (QOTs) have been recognized as extremely promising n-type and ambipolar OSCs with exceptionally high electron affinities and amphoteric redox behavior originating from strongly electron-withdrawing end-caping, dicyanomethylene and indophenine. Thieno[3,4-b]thiophene (TbT) is an electron-rich π-expanded moiety, and TbT-based organic small molecules and polymers have been investigated and displayed significant potential in OFETs and OPVs. Notably, TbT moiety confers on quinoids with remarkable chemical stability by enhancing quinoidal resonance of aromatic conjugated systems. we designed and synthesized a series of new quinoidal semiconductors TbTIs (1TbTI, 2TbTI and 3TbTI) with low-lying LUMO energy level and π-expanded conjugation by the combination of the electron-withdrawing indandione and the different number of quinoid-enhancing TbT unit. The quinoidal framework of TbTIs was verified by single crystal structure of 1TbTI. Organic thin-film transistors (OTFTs) based on 1TbTI, 2TbTI and 3TbTI displayed the ambipolar semiconducting property with progressive μ_e in an order of magnitude. As expected, 3TbTI possessed the superior transport behaviour with the highest μ_e of 0.164 $cm^2\ V^{-1}\ s^{-1}$. The correlation between device performance and molecular packing morphology were investigated.

Publication List

None

Solid-solid Crystal Conversion in Chiral Hybrid Perovskites with Paramagnetic-to-Ferromagnetic Transition

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Abstract

Hybrid organic-inorganic perovskites (HOIPs) are promising stimuli-responsive materials (SPMs) owing to their molecular softness and tailorable structural dimensionality. The design of mechanically responsive HOIPs requires an in-depth understanding of how lattice strain induces inter-molecular rearrangement or lattice reconstruction that leads to changes in physical properties. As opposed to achiral or racemic organic cations, chiral organic cations can potentially afford a new dimension in strain-responsive structural change. While chirality transfer from organic cation to inorganic lattice is known to influence chiral-optical properties, its effect on strain-induced phase conversion has not been explored. Herein, we demonstrate that mechanical strain induces a solid phase crystal conversion in chiral halide perovskite single crystals (R/S)-(4-Fluorophenyl)ethylamine)2CuCl4 from 0D isolated CuCl4 tetrahedral to 1D corner-sharing CuFCl5 octahedral framework via the incorporation of Cu···F interaction and N-H···F hydrogen bonding. This is the first demonstration of a perovskite structure with one of the X sites in BX6 octahedra occupied by fluorinated organic cation. The strain-induced crystal-to-crystal conversion involves the connection of neighbouring 0D CuCl4 tetrahedra via Cu2+-Cl--Cu2+ linkages, leading to a reduced bandgap and paramagnetic-to-ferromagnetic conversion. To demonstrate pressure-sensing properties, the 0D phase is dispersed in water-soluble poly(vinyl alcohol) (PVA) polymer, which can be applied to large-scale pressure-induced array display on fibrous spandex substrates via screen-printing method. A distinct thermochromic behavior is also observed in 1D phase, which can be applied to customized thermochromic stamping using a self-inking rubber stamp.

Publication List

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Strain and disorder stacking-induced breaking of odd-even effect in few-layer SnS

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Abstract

Two-dimensional ferroelectric SnS demonstrates unique potential in the application of optoelectronics, sensors and memories. Odd-even effect in SnS, where only odd-number layers are non-centrosymmetric and exhibit ferroelectricity, is broken by discovery of ferroelectricity in both odd and even-number layers, one explanation is AA stacking instead of AB stacking is adopted in few-layer SnS. However, the stacking order image is collected from transmission electron microscopy (TEM), indicating that the sample possibly change during preparation process and the image is selected from localized regions. Here we propose an alternative explanation that strain and disorder stacking break odd-even effect by scanning tunneling microscopy (STM). The STM characterization and transfer process are non-destructive as well as molecular beam epitaxy (MBE) growth is uniform. The lattice shows random orientation and gradually increase from 3.8 Å and 3.5 Å to 4.6 Å and 4.4 Å from 1st to 6th layer along the armchair and zigzag direction, respectively, causing ferroelectricity in even-number layers and suggesting disorder stacking and strain-induced breaking of odd-even effect. To further confirm the existence of ferroelectricity in different layers, STM images and KPFM were collected and quasi 1D nanoripples from 1st to 6th layer were observed, suggesting spontaneous polarization along the armchair direction. Our work provides a new understanding of the origin of layer-dependent ferroelectricity in SnS.

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

Fused Triangulene Dimer: Synthesis and Application for NIR Laser

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Abstract

Nanographenes have confirmed to be outstanding materials for optical devises due to their tunable energy gap and optical properties. By using varied aromatic stability, or using molecular symmetry to generate a myriad of structures with electronic transitions that span the UV, Vis, and near IR regions, nanographene molecules could designed for precise optical application such as laser materials and luminance materials. But developing efficient strategies to produce these nanographenes is a major obstacle. Besides, investigate the relationship between chemical structure of nanopgraphene such as molecule size, edge structure and their optical properties are also crucial for design nanographene with better laser performance. Herein, bottom-up approaches were used to synthesis a new kind nanographenes. Moreover, radical-radical coupling was also introduced to obtained target nanographnenes more effectively. This nanographene shows both low threshold and improved photostability as NIR organic laser.

Publication List

None

Chiral-twisted fused dibenzo-zethrene dimer and trimer

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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 electronic properties which is desirable for organic electronics. We have synthesized 2 novel zethrene-based diradicaloids with polyradical characters via nickel-catalyzed transannular cyclization, where a series of synthetic approaches and stabilization strategies were explored owing to their intrinsic instabilities. Their twisted structures were confirmed by X-ray crystallographic analysis, and they can be resolved by chiral high-performance liquid chromatography. On the basis of crystal analysis, total twisted angle is more than 180° (212°). Their electronic structure, physical properties and chemical reactivities were systematically studied by density functional theory calculations and various experimental methods such as electron spin resonance, UV–vis absorption, cyclic voltammetry and differential pulse voltammetry.

Publication List

None

A Graphyne Spoked Wheel

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Abstract

γ-Graphyne is an emerging carbon allotrope and synthesis of large-size atomically precise γ-graphyne fragments would be crucial to understand its distinctive properties. Herein, a long sought-after graphyne spoked wheel with six-fold symmetry was synthesized mainly through cobalt(0)-catalyzed cyclotrimerization of a triyne intermediate followed by twelve-fold intramolecular Stille coupling reactions. Its structure was unambiguously confirmed by X-crystallographic analysis, which also revealed a closely stacked dimer structure. NMR and theoretical analysis disclosed that fusion of six antiaromatic hexadehydro[12]annulene units led to decrease of local aromaticity of all seven benzenoid rings (particularly the central one), which is quite different from a graphene analogue, hexa-peri-hexabenzocoronene (HBC). Its optical and electrochemical properties are also different from HBC, showing allowed HOMO→LUMO electronic transition and facile electrochemical reduction. The study provided a new method for the synthesis of even larger γ-graphyne fragments and demonstrated the unique electronic properties of γ-graphyne as compared to graphene.

Publication List

B. Zhang, J. Wu et al., “A graphyne spoked wheel”. Chem. 2022.

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 an attractive route for the large-scale production of organic field-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 unclear.

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 directly measures the charge-induced optical transmission variation by probing the accumulated charge at the interface. It shows an advantage over the conventional characterization methods in probing charge carriers' accumulation and transportation behavior in OFETs.

Publication List

None

Fluorescent Lateral-Flow Immunoassays for SARS-CoV-2 Detection

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Abstract

Nowadays, due to the recent pandemic outbreak, associated diseases such as venous thromboembolism (VTE), are usually asymptomatic and difficult to detect, have caused many deaths worldwide. With home recovery become common setting for such virus infections, patients may face risk of missing the critical therapeutic window for associated diseases. Thus, the development of simple devices to reliably and rapidly perform diagnostic testing outside the laboratory has become vital for close monitoring of disease which is helpful for early intervention and lower mortality. In this regard, lateral flow immunoassay (LFIA) tests are one of the most promising assays for such point-of-care (POC) testing, allowing on-site monitoring of the disease biomarkers of patients in real-time, with the advantages of affordability, rapidness, and easiness to use. Here, by using fluorogens with aggregation-induced emission (AIE) characteristics, a highly adaptive yet sensitive fluorescent LFIA (FLFIA) detection platform has been established, which can be used to detect VTE and other diseases. In this project, FLFIA strips aiming for early detection of the COVID-19 that was based on the nucleic acid based LFIA. Poly(styrene-alt-maleic anhydride) (PSMA) with better antibody interaction is selected to encapsulate the dye, and it is observed that the antibody to dye ratio at 1:10 showed the best performance with 2 ng/mL detection sensitivity of SARS-CoV-2.

Publication List

None

Multi-functional interface modifiers for high efficiency perovskite solar cell

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Abstract

As the third-generation emerging photovoltaics, perovskite solar cell (PSC) has achieved considerable progress with certificated power conversion efficiency surpassing 25%, holding high 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. As the vertical p-i-n or n-i-p configuration of the device, interfacial loss of PSC origins from surface defect, morphology nonuniformity, unmatched energy level leading to reduced open circuit voltage (Voc) and fill factor (FF), thus insufficient performance and power conversion efficiency.

Interface modification through organic materials is promising for economical fabrication, solution processability, and enhanced charge transport of perovskite solar cell. Classic organic halide ammonium molecules with aliphatic or aromatic alkyl-spacer have achieved extensive success in 2D surface passivation, this field still lacks passivators with efficient multi-function for improving the PSC performance. Here, we designed a small molecule organic semiconductor embedded with aliphatic alkylammonium for interfacial engineering. Based on the interfacial modification between the perovskite surface and hole transport layer, the designed molecule has realized defect passivation and enhanced charge extraction for PSC.

Publication List

None

Organic Fluorophores with Chemiluminescence for Sensing and Imaging of Reactive Oxygen Species

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Abstract

Reactive oxygen species (ROS), as the natural byproduct of the normal metabolism of oxygen, play important roles in biological and chemical processes in the living organism. However, the excessive production of ROS would cause oxidative stress in the living systems, leading to many diseases, and it is significant to develop sensitive and selective platforms for detecting ROS in biological systems. In this regard, chemiluminescent (CL) materials are popularly considered as a novel tool for detection and imaging applications with the advantages of long luminescence lifetime, high penetration depth, and minimal interference from background autofluorescence as compared with fluorescence imaging. Yet, choices of chemiluminescence probes for ROS detections currently remain very limited.

Here, we aim to develop efficient near-infrared (NIR) emissive chemiluminescent probes for different ROS. In the first work, we developed a CL probe based on 1,2-dioxetane with the aggregation-induced emission (AIE) property through the intramolecular energy transfer process. It was found that the through-bond energy transfer system (CL-m-CN) obtained a better CL NIR emission than the through-space energy transfer system (CL+CN). CL-m-CN has demonstrated high selectivity towards singlet oxygen, proving its promising ability to detect and image intracellular singlet oxygen. Next, we design two luminophores, CL-o-BT and CL-o-CN, with the substituents at the ortho position of phenol to enhance NIR CL intensity. It was found that the CL intensity has been improved remarkably with simple phenol substitution. With its AIE property, CL-o-CN can yield brighter NIR CL which could last continuously last over 3000 min and can be utilized for intracellular imaging of singlet oxygen. Stable and highly efficient NIR CL probes for ROS-involved disease imaging will be developed for future works.

Publication List

None

Stable luminescent radicals applied in optoelectronic applications with doublet emission

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Abstract

As we all know, organic radicals, different from traditional closed-shell fluorescent molecules, can overcome spin statistics loss of charge recombination based on the spin-allowed doublet-doublet transition. Thus far, the reported stable luminescent organic radicals mainly have limited in TTM, PTM and BTM radicals, thus confining in orange-red, red and near-infrared OLEDs. It is difficult to enlarge the emission wavelength because of the natural narrow bandgap of these stable organic radicals. Therefore, this project focuses on exploring new series of stable luminescent radicals to provide a new platform to design organic radicals with expanded emissive wavelength.

Herein, we introduce xanthene, thioxanthene and selenoxanthene to trichlorobenzene, forming 9-(2,4,6-trichlorophenyl) -xanthene (TCP-O), 9-(2,4,6-trichlorophenyl)-9-thioxanthene (TCP-S) and 9-(2,4,6-trichlorophenyl) -selenoxanthene (TCP-Se). These molecules have electron acceptor-trichlorobenzene group which shields the reactive radical site, and electron donor-xanthene, thioxanthene and selenoxanthene which can enhance the delocalization of radical system, thus improving the stability of radicals. We find that this series of radicals produce green to orange emissions (527-607 nm) when change chalcogen atoms from oxygen to selenium, realizing a wide range of emission wavelength.

Furthermore, another advantage of organic radicals is that their optical functions can be finely regulated through chemical design. The project also introduces strong electron donor-benzomethoxy groups to the para-positions of xanthene, thioxanthene and selenoxanthene, forming an extended π-conjugated skeleton, to modulate energy gaps between the ground state and the excited states.

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.

Electron-Rich Ladder-Type Aromatics and Their Low Bandgap Conjugated Molecules and Polymers

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Abstract

Narrow bandgap organic materials are highly desirable in the fields of photovoltaics, photodetectors and field effect transistors, since this kind of material exhibits an excellent light absorption performance. 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.

At present, materials with the absorption in the NIR-II, especially the absorption wavelength greater than 1000nm are scarce. Considering the synthesis of electron-rich ladder-type aromatics is a powerful strategy to construct low bandgap materials, we are trying to provide effective methods for the design and synthesis of novel and high-performance electron-rich ladder-type aromatics.

Publication List

None

Convergent Synthesis of the Precursors to Thiophene-Based Quinoids

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Abstract

Quinoidal compounds (QCs) are a class of conjugated molecules characterized by low reorganization energies, low bandgaps (Eg) and deep-positioned lowest unoccupied molecular orbital (LUMO) energy levels and have found potential applications in various optoelectronics. The common route to a QC involves the introduction of terminal units (generally electron-deficient unit is used to stabilize the final quinoidal molecule) at the ends of aromatic core to form a precursor carrying two tertiary carbons via 1-2 steps followed by oxidation. A convergent (outside-to-center) route was adopted to synthesize the precursors of quinoidal compounds in high yields of 85-93%. With subsequent rearrangement/dehydroxylization and oxidation, a series of thiophene-based quinoids with indandione or oxindole terminal groups were successfully synthesized. This strategy shows high compatibility with versatile central and terminal units, leading to quinoidal compounds with tunable photophysical, electrochemical and charge transport properties.

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. We change the original alkyl chain from C4C6 to C10C12 to further increase its solubility and by adding the cyanide group at the end of both isoindigo derivatives core to identify the influence of the heteroatom. 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 polymer for photochemical energy conversion

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Abstract

Recently, the energy crisis becomes a global issue. We are urgently seeking advanced energy conversion technology and eco-friend energy sources. Solar-to-chemical energy conversion is a promising channel for energy conversion and storage, and photocatalytic hydrogen evolution is the main process. However, this process is facing some drawback: (1) low quantum efficiency; (2) scavenger reagent is needed; (3) self-decomposition of catalysts by photodegradation.

Herein, we choose hydrogen peroxide photogeneration as the energy conversion process. The liquid product can avoid explosion of gas, and the only reagent for the reaction is water. We construct a photocatalytic system using thiophene-basd polymer as the photocatalyst. The suitable energy band level to the high efficiency of the catalyst.

Publication List

None

Hybrid Copper Halide Perovskites with Ferroelectric and Ferromagnetic Property 2023 NUS-TJU PhD Workshop

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Abstract

Ethanolammonium copper chloride (EOA2CuCl4) and BPA2CuCl4-xBrx (where BPA is 3-bromopropylammonium) perovskite single crystals were synthesized via solvent evaporation of ethanol and methanol respectively. EOA2CuCl4 shows potential ferroelectricity, while BPA2CuCl4-xBrx exhibits ferromagnetism at low temperature. In EOA2CuCl4, the hydroxyl group of organic cation provides hydrogen bonding between organic layer of RP copper halide perovskites and leads to the spontaneous polarization in EOA2CuCl4. A phase transition of EOA2CuCl4 from I4/mmm to Cc was verified by Differential Scanning Calorimetry (DSC) and single Crystal X-ray Diffraction (SXRD), which corresponds to paraelectric-to-ferroelectric phase transition with AIZU notation of 4/mmmFm. Besides, domain patterns of EOA2CuCl4 were visualized by Piezoresponse Force Microscopy (PFM). As for BPA2CuCl4-xBrx, its soft magnet nature was verified by magnetization hysteresis measurement. John-Teller (JT) distortion and superexchange accounts for the ferromagnetism in copper halide perovskites. Furthermore, bromide doping was found to effectively reduce the bandgap of perovskites and it also influences the superexchange between Cu2+ and improves the Curie temperature. Two-dimensional (2D) ferroelectric EOA2CuCl4 is promising for nonvolatile memory unit to be integrated in microelectronics, while semiconducting BPA2CuCl4-xBrx ferromagnetic perovskites can be applied in spintronics.

Publication List

None

A COF membrane based on electrospinning for ultra-fast separation of oil/water emulsion

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Abstract

Oily water, a very common pollution all around the world, has become one of the most serious global issues. There are many oily water resources, including petroleum refineries, mining exploration, food processing, metal/steel industries, and cosmetics industries. Taking petroleum refineries as an example, oil leakages happen frequently during the oil exploring process. That could result in serious wastage of the limited oil resources as well as serious environmental contamination issues. Therefore, it is very vital to take effective measures to improve the separation efficiency and flux of oil-water mixtures.

Up to now, many kinds of materials have been used to make oil-water separation membranes, such as Graphene, SiO2, MOFs, COFs, and so on. As a distinct type of porous crystalline polymer connected by reversible covalent bonds, COFs recently get keen attention from scientists. The highly ordered, porous, and designable frameworks enable COFs to be used for all kinds of applications, including energy storage, gas separation, catalysis, sensing, etc. Herein, we aim to prepare a hydrophobic electrospun COF membrane for oil/water separation. The COF particles were mixed with PVDF/DMF solutions in a certain proportion, and then hydrophobic composite membrane ware made by electrospinning.

Publication List

None

π-conjugated macrocycle and organic electrode materials

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Abstract Text

Aromaticity is a key concept to understand the electronic properties of π-conjugated molecules for the development of application of π-conjugated organic materials in optoelectronics and energy systems. Hückel, Möbius and Baird's rules have been proposed to realize the aromaticity. Strictly, these rules are mainly applied for monocyclic systems and many porphyrinoids systems, while reports on polycyclic aromatic hydrocarbons (PAHs) subjected to these rules are limited. The aromaticity in polycyclic π-conjugated systems is more complicated, where competition between local aromaticity and global aromaticity is considered. For example, kekulene was found that its π-electrons were localized in individual benzene-type rings rather than delocalized within entire skeleton. Therefore, researches on polycyclic π-conjugated systems, especially π-conjugated macrocycles, are of importance to further understand the aromaticity. Herein, all-benzenoid π-conjugated perylene-based and naphthalene-based macrocycles were designed, with different current directions within the inner ring and outer ring in the anisotropy of the induced current density (AICD) plot.

Publication List

None

Thienopyrazine-based Macrocycle and Oligomer with Diradicaloids

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Abstract Text

The aromaticity reversal in the lowest triplet excited state (so-called Baird's rule) is conceived

much attention due to supplies important insight into photo-reactivity/stability and the application to the photoactive materials and photosynthetic mechanism but this kind of molecule synthesis is very challenging. Herein, the synthesis of thienopyrazine-based macrocycle is designed and described. In the macrocycle structure, the pyrazinyl group which contains the electronegative nitrogen atom, tends to form an aromatic structure like a benzene ring and displays macrocyclic π-electron delocalized quinones structure containing 48 π electrons. The calculated diradical characters is 19.2%. In addition, the synthetic routes of thienopyrazine-based oligomers are also designed, they are theoretically predicted that they would show an increase of diradical character with the extension of chain length. The calculated diradical characters of different thienopyrazine-based oligomer with different chain length are 1.8%, 6.2%, 10.8% respectively. The macrocycle and thienopyrazine-based oligomers are expected to be synthesized in the following work.

Publication List

None

Open-shell polymer

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Abstract

Most organic semiconductors or solar cells have closed-shell electronic structures. However, there are research showed open-shell character emanating from design paradigms such as narrowing the bandgap and controlling the quinoidal-aromatic resonance of the π-system. One fundamental challenge is to understand the relation between open-shell electronic structure and the physicochemical properties or optical functionality. This work mainly focuses on synthesis Donor-Acceptor conjugated polymers and oligomer, based on naphthothiadiazole and other building blocks. Benzothiadiazole and naphthothiadiazole are good electron acceptor with strong diradical character. Designed building blocks and synthesized for making oligomer and polymer. For the acceptor units are usually electron deficient that lower the band gap combine with electron donating units, enhance the charge mobility of polymer and oligomer. Theoretically, the D-A based polymer will exhibit better photo-physical performance than other organic solar cells. This D-A polymer may have potential of organic semiconductors or solar cells. Various characterization methods will be used, such as Nuclear magnetic resonance, electron spin resonance, single-crystal X-ray, computer simulation.

Publication List

None

P-block metal-based nanostructure for efficient CO2 electroreduction

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Abstract

The efficient conversion of CO2 to value-added products represents one of the most attractive solutions to mitigate climate change and tackle the associated environmental issues. In particular, electrochemical CO2 reduction into to fuels and chemicals via renewable energy as sustainable technologies has garnered tremendous interest over the last decades. Among all these value products, formic acid is considered one of the most economically vital CO2 reduction products, revealing the great potential for real-life applications. P-block metals (especially Bi, Sn, In, and Pb) have been extensively researched and recognized as the most efficient catalytic materials for the electrochemical reduction of CO2 to formate. Despite the remarkable progress, the future implementation of this technology at the industrial-scale hinges on the ability to solve remaining roadblocks.

In this work, we designed and synthesized a bismuth-based superlattice as a model electrocatalyst to study the structure-performance correlation. The superlattice consists of an active layer and a conductive layer, where the active layer provides massive active sites, while the conductive layer can speed up electron transfer. The Faradaic efficiency of formate can be tuned by adjusting the ratio of active layer to conductive layer.

Publication List

None

Low temperature STM investigation of self-assembly and reaction of C8-BTBT

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Abstract Text

The self-assembly, electronic properties and possible reactions of 2,7-dioctyl benzothieno[3,2b]benzothiophene (C8-BTBT) on Au (111), Ag (111) and Cu (111) were investigated with scanning tunneling microscope (STM).

Organic semiconductors (OSCs) have been intensively studied as promising candidates for active layers of organic field effect transistors (OFETs) with extraordinary properties, such as economically low-cost, mechanical flexibility, and light weight. The carrier mobility of OSCs, one of the most important parameters for applications, is relatively low compared to that of traditional inorganic semiconductors, such as silicon. To improve the charge mobility, researchers have investigated considerable methods. C8-BTBT has been approved to have a remarkable high carrier mobility. Au, Ag and Cu are all important electrode materials in OFETs. It is meaningful to investigate the interactions, assembly mode, and electronic properties of C8-BTBT with these metals.

Publication List

None

Field-induced organic light emitting diodes driven by alternating current

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Abstract Text

Electroluminescent devices based on organic materials have attracted extensive attention due to their many advantages, such as low cost, easy fabrication, wider viewing angle, high resolution, better contrast ratio. The current electroluminescent devices are mainly driven by direct current, while the alternating current as one of two mainstream power supply modes provided a new strategy for electroluminescent devices and possess its unique advantages, such as a variety of device structures, more driving methods, which provide a feasible solution for solving common problems in OLEDs, such as charge accumulation and efficiency roll-off. In this work, we constructed asymmetric AC devices based on commonly used organic materials to realize high-performance light-emitting devices. We first constructed an organic light-emitting device with commercial light-emitting materials Alq3, demonstrated alternating current luminescence, and analyzed the factors that affect the performance of the device to understand the mechanism behind its operation.

Publication List

None

Two-photon-excited organic room temperature phosphorescent materials

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Abstract

Ultralong room temperature phosphorescent (RTP) materials could continue to emit light for several seconds to hours after the excitation light source is removed, which could effectively reduce the interference of background light and excitation light, which can greatly improve the signal-to-noise ratio and the accuracy of bio-imaging. Two-photon absorption (TPA) molecule can absorb two photons simultaneously during photoexcitation. Therefore, the excitation wavelength in such system could be significantly redshifted to even the near-infrared (NIR) range, which contributes to higher spatial resolution, less phototoxicity and deeper tissue penetration. In this project, we are trying to develop high-efficiency two-photon excited organic phosphorescent materials that combine both the advantages of TPA and RTP. Such material may be able to achieve both instantaneous excitation and sustained emission, which significantly reduce the damage of laser irradiation in bio-imaging. We design several molecules in which phenothiazine 5,5-dioxide group acted as electron donor and dimethyl isophthalate derivative acted as acceptor. Donors and accepters are linked by alkyl chain. The presence of the alkyl chain breaks the D-A conjugation and restricts the intramolecular charge transfer. Therefore, during crystallization, donor–acceptor interactions between molecules may be the main driving force and contribute to intermolecular charge transfer and TPA properties. Besides, we also try to introduce difluoroboron β-diketonate group to improve the TPA and RTP properties.

Publication List

None.

Water Induced Room Temperature Phosphorescence

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Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, China
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Abstract

Recently, pure organic room temperature phosphorescent (RTP) luminescent agent has attracted more and more attention due to their wide application in various fields such as anti-counterfeiting, sensors, biological imaging, and OLED. For further development of RTP materials, it is important to deeply understand its internal mechanism. Therefore, due to the great efforts of scientists, a series of corresponding mechanisms have been proposed, such as H-aggregation, strong intermolecular hydrogen bond, π-πstacking, intermolecular n-π electron coupling, etc.

Stimulus-response characteristic is a hot topic in the field of RTP luminescence, that is, external stimuli including water, oxygen, and organic gases can induce, quench or change the emission behavior of RTP materials. The research of pure organic RTP materials with stimulus-response characteristics has attracted more and more attention because of their broad application prospects. In previous work, many stimulus-response RTP emission phenomena have been found. For example, light activation, volatile organic compounds (VOC) activation, water vapor quenching, oxygen quenching, etc. Recently, we found an RTP phenomenon completely opposite to water quenching, that is, the material without RTP emission can have RTP emission through the stimulation of water. In addition, this emission can be completely quenched after heating. This reversible stimulus-response process can be repeated more than 20 times. This phenomenon may help us better understand the emission mechanism of RTP composites as well as be applied for programmable information storage and encryption.

Publication List

None

The synthesis and characterization of imide-containing ladder type building blocks

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Department of Chemistry, National University of Singapore, Singapore

Abstract

The fundamental molecular design of organic semiconductor has attracted extensive attention recently due to the rapid progress of organic electronics. Development of new π-conjugated building blocks plays an important role in the evolution of novel organic/polymeric semiconducting materials. Various imide-based building blocks, such as perylene diimide (PDI) and naphthalene diimide (NDI), have been incorporated into organic semiconductors, leading to the development of a novel class of organic semiconductors with excellent device performance, due to their strong electron-withdrawing nature lowering LUMO levels, facilitate electron injection, and stabilize injected electrons. In addition, since charge transport occurs in π-conjugated system, coplanar backbone in n-type building blocks is beneficial to enhancing electron mobility. However, researches of n-type building blocks have rarely focused on fused-ring ladder type structures. To further explore new n-type semiconducting materials for higher electron mobility, we herein design novel electron deficient fused-imide building blocks and their conjugated polymers and apply them in OFETs. In my recent study, a fused-imide building block, p-terphenylenediimide (PPI) with five fused rings is synthesized.

Publication List

None.

Unraveling the Stability-Morphology of Nonfullerene Organic Solar Cells

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Department of Chemistry, National University of Singapore, Singapore

Abstract

Organic solar cells (OSCs) based on nonfullerene electron acceptors (NFAs) have achieved an impressive power conversion efficiency (PCE) of 18% for single-junction devices over the past few years. However, the study on the long-term stability and degradation mechanism of NFA-based OSCs is far behind than that of fullerene-based OSCs, which is crucial for the commercial applications of the technology.

OSC devices are complicated multilayer structures where each component may cause degradation for different reasons. The morphology and molecular structure of organic semiconductors can be easily altered under certain environmental stress conditions such as oxygen and water, photon illumination, and thermal treatment. The interlayer is another crucial consideration for the stability of NFA-based OSCs. PEDOT:PSS and ZnO are the most widely used interlayers but suffer from high reactivity with active layers.

Our group has developed self-compensated heavily-doped polymers, which exhibit ultrahigh and ultralow work functions. With these materials employed as HTL and ETL, ohmic hole and electron contacts can be achieved in OSCs. With this regard, we explore the stability of NFA-based OSCs by replacing the PEDOT:PSS and ZnO with the self-compensated heavily-doped polymers and further research the relationships of the chemical structure-physicochemical properties-morphological metrics-device performance of OSCs when the devices are exposed under a wide range of conditions.

Publication List

None

Workshop Schedule

Center 2: Organic Chemistry			
Symposium Chair: Lin Zhikeng			
Morning Session (Jan 7)			
	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	**Asymmetric Synthesis of Indole-based Axial N-N Chiral Compounds through Allylic Alkylation**	Lu Yixin
9:40-10:00	Lin Zhikeng	**Desymmetrisation of 5-substituted-1,3-diones**	Zhao Yu
10:00-10:20	Gao Yaru	**Enantioconvergent Amination of Alcohols via Dynamic Kinetic Resolution: Access to Chiral C2- and C3-Substituted Benzomorpholines**	Zhao Yu
10:20-10:40	Pan Jiaoting	**Access to chiral eight-membered heterocycles via Pd-catalyzed enantioselective (4 + 4) cycloaddition of azadienes**	Zhao Yu
10:40-11:00: Break			
Session Chair: Lin Zhikeng			
11:00-11:20	Dong Xiaohan	**Enantioselective Synthesis of α-Quaternary Amino Acid by Michael Addition and Consequent Radical Cross-Coupling with Sulfones**	Ma Jun'an & Lu Yixin
11:20-11:40	Yuan Ye	**Six-membered silacycles synthesis from photo-induceded multifluorinated arenes C(sp2)-F activation**	Ma Jun'an & Wu Jie
11:40-12:00	Zhao Taoqian	**Copper-Catalyzed Enantioselective Hydroboration of Difluoromethylated Internal Alkenes**	Ma Jun'an & Ge Shaozhong

Lunch Break			
Afternoon Session (Jan 7)			
	Presenter	**Title**	**Supervisor**
Session Chair: Huang Qingqin			
14:00-14:20	Huang Qingqin	**Nickel-Hydride-Catalyzed Diastereo- and Enantioselective Hydroalkylation of Cyclopropenes**	Lu Yixin
14:20-14:40	Guo Jiami	**Light-Induced Phosphine-Catalyzed Asymmetric Functionaliza-tion of Benzylic C–H Bonds**	Lu Yixin
14:40-15:00	Sun Yuli	**Asymmetric Hydrophosphinylation of Maleimides: Facile Access to N-N Axially Chiral Compounds**	Lu Yixin
15:00-15:20	Zou Gongfeng	**Divergent Access to Medium-sized Heterocycles Containing Z/E-Controllable Trisubstituted Alkenes through Pd-catalyzed cycloaddition**	Zhao Yu
15:20-15:40	Diao Huanlin	**Iridium-Catalyzed Enantioconvergent Borrowing Hydrogen Annulation of Racemic 1,4-Diols with Amines**	Zhao Yu
15:40-16:00: Break			
Session Chair: Huang Qingqin			
16:00-16:20	Liu Yufeng	**Borrowing Hydrogen Reaction between Allylic Alcohol and Amine**	Zhao Yu
16:20-16:40	Zhang Zhiqi	**Difluoromethylation of Unactivated Alkenes Using Freon-22 through Tertiary Amine-Borane Triggered Halogen Atom Transfer**	Ma Jun'an & Wu Jie
16:40-17:00	Zhai Yixuan	**Cobalt-catalyzed Asymmetric hydrodefluorinative Cyclization of Fluoroalkyl-Substituted 1,6-Enynes**	Ma Jun'an & Ge Shaozhong
17:00-17:20	Luo Xiaohua	**Nickel-catalyzed Enantioselective Diarylation of Alkenes**	Ma Jun'an & Koh Ming Joo

Morning Session (Jan 8)			
	Presenter	**Title**	**Supervisor**
Session Chair: Zeng Hao			
9:00-9:20	Sun Yuli	**Copper Catalyzed Atroposelective Synthesis of Axially Chiral Styrenes**	Lu Yixin
9:20-9:40	Zhou Xueting	**Asymmetric Oxo-Hydroarylation of Alkynes for Efficient Synthesis of Diarylmethanes via Photo-Driven Chiral Phosphoric Acid Catalysis**	Lu Yixin
9:40-10:00	Mi Fen	**Phosphine-catalyzed ring-opening of azetidines via C-N bond activation**	Lu Yixin
10:00-10:20	Zeng Hao	**Photo-Induced Direct Alkylidenation of C-H Bonds and C-C Bond**	Ma Jun'an & Wu Jie
10:20-10:40	Tian Yuchen	**Transition Metal Catalyzed Asymmetric Hydroboration of Internal Alkenes**	Ma Jun'an & Ge Shaozhong
10:40-11:00: Break			
Session Chair: Zeng Hao			
11:00-11:20	Liu Chi	**Construction of P-Stereogenic Center through Long-Range Recognition**	Ma Jun'an & Zhu Ye
11:20-11:40	Wang Luoyu	**Chiral Acid-Catalyzed Atroposelective Indolization Enables Access to 1,1’-Indole-Pyrroles and Bisindoles Bearing a Chiral N-N Axis**	Zhao Yu
11:40-12:00	Ke Yaming	**Palladium-Catalyzed Cycloaddition Using 8-Azahptafulvenes**	Zhao Yu
12:00-12:20	Shi Lin	**Enantioselective Synthesis of 2,2-Disubstituted Tetrahydrofurans and Tetrahydropyrans via Pd-catalyzed Intramolecular Allylic Substitution**	Zhao Yu
12:20-12:40	Zhu Kun	**Energy-Transfer-Enabled Regioconvergent Alkylation of Azlac-tones via Photocatalytic Radical-Radical Coupling**	Lu Yixin
End of Center 2: Organic Chemistry Symposium			

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

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Abstract Text

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.

Asymmetric Synthesis of Indole-based Axial N-N Chiral Compounds through Allylic Alkylation

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Abstract Text

Axial chiral compounds are a kind of privileged scaffold widespread exiting in natural products and biologically active molecules including vancomycin, streptonigrin and michellamines. However, lots of prepared axially chiral compounds are restricted to those having a carbon-carbon (C-C) or carbon-nitrogen (C-N) axis. On the contrary, the catalytic atroposelective synthesis of N-N axially chiral compounds are underdeveloped even though the N-N axial chiral scaffolds also constitute the core structures of natural products, bioactive molecules and chiral catalysts. Therefore, our group developed the synthesis of a new class of N-N axially chiral indole scaffolds through asymmetric allylic alkylation. A new member of N-N atropisomers with potential applications are developed with excellent enantioselectivity.

Publication List:

None

Energy-Transfer-Enabled Regioconvergent Alkylation of Azlac-tones via Photocatalytic Radical-Radical Coupling

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Abstract Text

C-4-selective functionalization of azlactones represents an important approach to access α,α disubstituted unnatural α amino acids, which has been extensively investigated in the past decades. However, vast majority of such transformations are two-electron transfer reactions, and examples based on radical processes are rare. Herein, leveraging on persistent radical effect (PRE), we develop the first photocatalytic energy transfer (EnT)-enabled regioconvergent alkylation of azlactones with redox-active esters via radical-radical couplings. This strategy is extended to the utilization of simple alkanes as the radical precursors whereby the aryl redox-active esters exert a dual role of an oxidant and a hydrogen atom transfer (HAT) agent. Notably, the excited-state Ir(III) photocatalyst enables selective activation of the un-wanted imine products through triplet energy transfer, delivering C-4-functionalized azlactones with high regioselectivity. Both experimental investigations and DFT calculations on the reaction mechanism were performed, supporting EnT-enabled regioconvergent photocatalytic radical-radical coupling reaction pathways.

Publication List:

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

Desymmetrisation of 5-substituted-1,3-diones

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Abstract Text

Desymmetrisation of readily available *meso* 1,3-diones has been applied to access a variety of chiral ketones, which represents important intermediates in the synthesis of drugs and natural products. During the past decades, intramolecular enantioselective aldol condensation represents the most established strategy for desymmetrisation of 1,3-diones with pre-installed functionalised side chain. Only in recent years, relatively simple transformations, including enantioselective monoreduction and intermolecular condensation with amines or hydrazines, have been introduced. In this work, we aimed to achieve the desymmetrisation of 1,3-diones by imine condensation in order to access chiral ketones bearing a β-stereogenic centre with commercially available substrates and catalysts. With amines bearing different functional groups, further derivatisation could be conducted to broaden the synthetic diversity of this transformation.

Publication List:

None

Enantioconvergent Amination of Alcohols via Dynamic Kinetic Resolution: Access to Chiral C2- and C3-Substituted Benzomorpholines

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Abstract Text

Enantioconvergent transformations via dynamic kinetic resolution (DKR) represent a significant strategy in stereoselective synthesis, offering the powerful capability of converting readily accessible, racemic starting materials to value-added enantioenriched products. One particularly intriguing yet challenging class of DKR reactions entail the establishment of a single pre-existing stereocenter in the substrate. Very few examples of this type are known in the literature, all focusing on asymmetric (transfer) hydrogenation or reductive amination to produce simple acyclic alcohols or amines bearing β-stereogenic center. If this type of DKR can be applied to N-heterocycle synthesis, it will be highly desired for preparing valuable enantioenriched heterocycles with substitution patterns. Our group has a continue interest on the exploration of enantioconvergent borrowing hydrogen for *N*-heterocycle synthesis, we were attracted to benzomorpholines that are widely present in bioactive compounds and drugs. Despite extensive efforts in method development, achieving high enantiocontrol in the preparation of benzomorpholines, and especially the C2-substituted variants with stereocenter away from the amine moiety, still represents a significant challenge.

Herein, we report an unprecedented DKR strategy for the enantioconvergent synthesis of C2-substituted benzomorpholines from readily available amino alcohols via redox-neutral amination. The identification of effective cooperative catalysis using iridium and iron was key for achieving this enantioselective transformation. Intriguingly, the nitro precursor to the amino-primary alcohol substrate could also be converted to the alternative amino-secondary alcohols through a Smiles rearrangement. The enantioconvergent amination of this alternative class of substrates was also established using commercially available iridium catalyst to produce chiral C3-substituted benzomorpholines. Our method thus results in a divergent enantioconvergent preparation of both C2- and C3-subsituted benzomorpholines from common precursors.

Publication List:

Gao, Y.; Wang, L.-Y.; Zhang, T.; Yang, B.-M.;* Zhao, Y.* *Angew. Chem. Int. Ed.* **2022**, e202200371.

Access to chiral eight-membered heterocycles via Pd-catalyzed enantioselective (4 + 4) cycloaddition of azadienes

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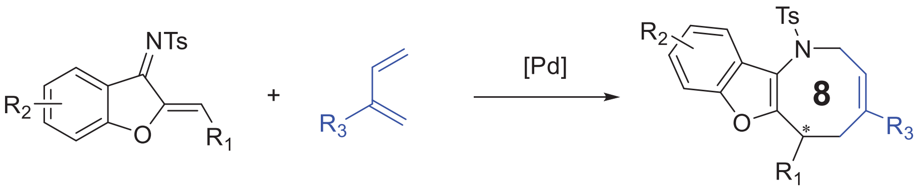
Abstract Text

Medium-sized rings (8 to 11-membered rings) are important scaffolds in natural products and bioactive molecules. However, there has been a lack of general, efficient stereoselective access to these structures due to the negative entropy effect and transannular interactions. Our group has focused on the development of enantioselective formal cycloaddition reactions to achieve efficient syntheses of versatile medium-sized rings. In particular, we reported a series of Pd-catalyzed (4 + n) cycloaddition of azadienes to deliver enantioenriched 9 to 10-membered N-heterocycles. Herein, we report a Pd-catalyzed highly enantioselective (4+4) cycloaddition of azadienes and simple 1,3-dienes for eight-membered heterocycle synthesis, through a novel Pd (0)-activation of simple dienes as a π-Lewis base.



♦Simple 1,3-dienes as substrates
♦Pd as a π-Lewis base catalyst
♦29 examples, up to 95% ee

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.

Enantioselective Synthesis of α-Quaternary Amino Acid by Michael Addition and Consequent Radical Cross-Coupling with Sulfones

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Abstract Text

Quaternary centers are important building blocks in biological and physiological area. Among them, construction of α-Quaternary amino acids is much attractive owing to their ability to induce helical peptide configuration and stabilize proteases. However, the synthesis of such structures still remains challenges as it usually requires harsh conditions and tedious steps. Considering radical cross-coupling is a useful strategy to construct new C-C bonds, introducing redox active block into designed structure might provide a convenient pathway to desired product. Herein, I will mainly introduce a novel reaction mode to access useful α-quaternary amino acid structure by combination of sulfone addition chemistry with radical coupling reactions.

Publication List:

None

Six-membered silacycles synthesis from photo-induceded multifluorinated arenes C(sp2)-F activation

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Abstract Text

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. Silicon is the second most abundant element in the earth crust. Compared with carbon, the silicon atom has a ’s larger covalent radius, less electronegativity, and extra orbitals. These distinct properties make organosilicon compounds widely applicable in organic synthesis, pharmaceuticals, agrochemistry, and material sciences. Inspired by the mode of activation of the Si–C bonds in silicon-based cross-coupling reaction. Here we prose a project involving the two stepwise hydrogen atom transfer of silane, and the silane radical added to the C(sp^2)-F bond. If successful, the reaction is expected to provide facile access to sila-multifluoro benzo silacycles from readily available substrates.

Publication List:

None

Copper-Catalyzed Enantioselective Hydroboration of Difluoromethylated Internal Alkenes

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Abstract Text

Catalytic asymmetric hydroboration of fluoroalkylated alkenes is a straightforward approach to access chiral small molecules possessing both fluorine and boron atoms. However, enantioselective hydroboration of fluorinated alkenes without fluorine elimination has been a long-standing challenge in this field. Herein, we report a copper-catalyzed hydroboration of difluoromethylated internal alkenes with high levels of regio- and enantioselectivities. The judicious choice of native carbonyl directing group, copper hydride system, and suitable bisphosphine ligand play in concert together to suppress the unwanted β-fluoride elimination. This atom-economic protocol provides a practical synthetic platform to obtain a wide scope of enantioenriched secondary boronates bearing the difluoro-carbonyl moieties under mild conditions. Synthetic applications including functionalization of biorelevant molecules, versatile functional group interconversions, and preparation of difluoroalkylated Naproxen and difluorinated Terfenadine are also demonstrated, which suggested this method is a powerful strategy to introduce fluorine atom into chiral drugs. We anticipate this unprecedented strategy will find broad applications in both synthetic chemistry and drug development.

Publication List:

None

Nickel-Hydride-Catalyzed Diastereo- and Enantioselective Hydroalkylation of Cyclopropenes

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Abstract Text

Cyclopropanes are structural motifs that are widely present in natural products and bioactive molecules, and they are also tremendously useful building blocks in synthetic organic chemistry. Asymmetric synthesis of cyclopropane derivatives has been an intensively researched area over the years, but efficient asymmetric preparation of alkylcyclopropane scaffolds remains a challenging topic. Herein, we report a nickel-hydride-catalyzed enantioselective and diastereoselective hydroalkylation of cyclopropenes for facile synthesis of chiral alkylcyclopropane motifs. The reported method is efficient and versatile, taking place under mild reaction conditions, and having broad applicability and excellent functional group tolerance.

Publication List:

Q. Huang, Y. Chen, X. Zhou, L. Dai, Y. Lu. *Angew. Chem. Int. Ed.* **2022,** *61,* e202210560

Light-Induced Phosphine-Catalyzed Asymmetric Functionaliza-tion of Benzylic C–H Bonds

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Abstract Text

Despite rapid development in the past two decades, there are however some unsolved synthetic challenges in the field of phosphine catalysis. In this report, through photo-induced activation of *ortho*-alkyl aromatic ketones, we achieved highly enantioselective functionalization of substrates bearing a benzylic C–H bond for the first time. In the presence of amino acid-derived bifunctional phosphine catalysts, a range of benzylic allylation products were obtained in good yields and with excellent enantioselectivities. The strategy disclosed herein offers new insight into the activation and functionalization of pronucleophiles containing less acidic C–H bonds in the domain of phosphine catalysis and beyond.

Publication List:

Guo J., Shen Z.-A., Zhou X., Dai L.* and Lu Y*. Light-induced phosphine-catalyzed asymmetric functionalization of benzylic C–H bonds. *Sci. China Chem*., **2023**, *66*, doi: 10.1007/s11426-022-1406-y.

Asymmetric Hydrophosphinylation of Maleimides: Facile Access to N-N Axially Chiral Compounds

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Abstract Text

Axially chiral molecules widely exist in biologically active compounds, natural products, and pharmaceuticals. They also severed as privileged scaffolds in organocatalysts and chiral ligands. In the past few decades, the construction of C-C and C-N axially chiral compounds have been well-studied. However, there are rare examples and methods to synthesize N-N axially chiral compounds due to the low rotational barrier energy. Our group has intensively interests in construction of axial chirality with the low rotational barrier energy. Herein, we disclosed a new method to access the N-N axially chiral molecules via organocatalyzed hydrophosphinylation of maleimides. The features of our reaction: 1) containing axially and central chiralities, 2) remote control of the N-N bond axial chirality, 3) construction of chiral C-P bonds, 4) challenging control of diastereoselectivity.

Publication List:

None

Divergent Access to Medium-sized Heterocycles Containing Z/E-Controllable Trisubstituted Alkenes through Pd-catalyzed cycloaddition

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Abstract Text

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

Iridium-Catalyzed Enantioconvergent Borrowing Hydrogen Annulation of Racemic 1,4-Diols with Amines

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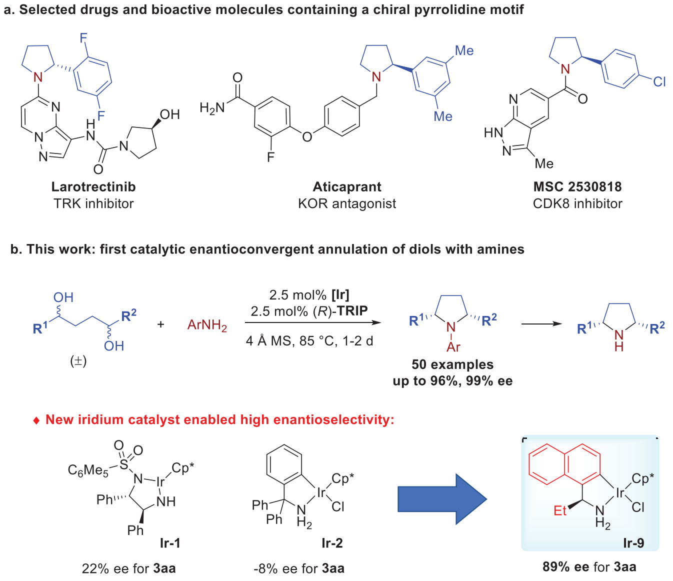
Abstract Text

We present an enantioconvergent access to chiral N-heterocycles directly from simple racemic diols and primary amines, through a highly economical borrowing hydrogen annulation. The introduction of a new iridacycle catalyst was the key for achieving high efficiency and enantioselectivity in the one-step construction of two C-N bonds. This catalytic method enabled a rapid access to a wide range of diversely substituted enantioenriched pyrrolidines including key precursors to valuable drugs such as Aticaprant and MSC 2530818.



Publication List:

None

Borrowing Hydrogen Reaction between Allylic Alcohol and Amine

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Abstract Text

Chiral amines are widely found in natural products and drugs, traditional synthetic methods for chiral amines usually produce equivalent pollutants. Although asymmetric hydrogenation method has higher atomic economy and less pollution, high-pressure hydrogen is flammable and potentially explosive. In comparison, borrowing hydrogen reaction has many advantages, such as high atomic 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. we also obtained high diastereoselectivity and enantioselectivity. Next, we may try to synthesize various types of heterocyclic structures.

Publication List:

None

Difluoromethylation of Unactivated Alkenes Using Freon-22 through Tertiary Amine-Borane Triggered Halogen Atom Transfer

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Department of Chemistry, National University of Singapore, Singapore

Abstract Text

The application of abundant and inexpensive fluorine feedstock sources to synthesize fluorinated compounds is an appealing yet underexplored strategy. Here, we report a photocatalytic radical hydrodifluoromethylation of unactivated alkenes with an inexpensive industrial chemical, chlorodifluoromethane ($ClCF_2H$, Freon-22). This protocol is realized by merging tertiary amine-ligated boryl radical-induced halogen atom transfer (XAT) with organophotoredox catalysis under blue-light irradiation. A broad scope of readily accessible alkenes featuring a variety of functional groups, drug and natural product moieties, could be selectively difluoromethylated with good efficiency in a metal-free manner. Combined experimental and computational studies suggest that the key XAT process of $ClCF_2H$ is both thermodynamically and kinetically favored over the hydrogen atom transfer (HAT) pathway owing to the formation of a strong boron-chlorine (B–Cl) bond and the low-lying antibonding orbital of the carbon-chlorine (C–Cl) bond.

Publication List:

Zhi-Qi Zhang,# Yue-Qian Sang,# Cheng-Qiang Wang, Peng Dai, Xiao-Song Xue, Jared L. Piper, Zhi-Hui Peng, Jun-An Ma,* Fa-Guang Zhang,* and Jie Wu*. *J. Am. Chem. Soc*. **2022**, *144*, 14288–14296.

Cobalt-catalyzed Asymmetric hydrodefluorinative Cyclization of Fluoroalkyl-Substituted 1,6-Enynes

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Abstract Text

The introduction of fluorinated moieties into organo-compounds represents one of the most significant subjects in organic synthesis as the methodology tremendously changes the physiochemical and pharmacological properties. The unique electronic nature and biological affinity have allowed organofluorides to plays an active role in pharmaceutical and agricultural industries. Among them, the gem-difluoro vinyl species have drawn enormous attention in account of their electronic resemblance with the corresponding carbonyl isomers. The ability to maintain electronic property yet profoundly improve the bioactivity and target specificity of the carbonyl parental molecules has been proven a powerful tool in drug discovery. Here, we present a cobalt catalyzed asymmetric hydrodefluorinative cyclization of fluoroalkyl-substituted 1,6-enynes to access chiral five-membered lactones with gem-difluoro vinyl functional motif. So far, the reaction can tolerate a wide range of mono- or di-substituted 1,6-enyne with decent enantioselectivity (80%-92% ee) and good yield. Mechanism study indicated a Co-F elimination process which constitute the desired product. The transformation and in-depth mechanism interpretation is under progress.

Publication List:

None

Nickel-catalyzed Enantioselective Diarylation of Alkenes

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Abstract Text

Dicarbofunctionalization of alkenes is one of the most important classes of chemical transformations. In this field, metal-catalyzed enantioselective diarylation of alkenes can rapidly construct tertiary carbon centers and vicinal disubstitution patterns, so that these reactions are often used to synthesize complex drug molecules and natural products. To date, a number of works have been done for the asymmetric diarylation of alkenes, but there are still have some limitations of previous works. Most developed methods employed either styrenes, N-acyl enamines or aryl-1,3-dienes as substrates and scope is relatively limited. Furthermore, reported methods are only capable of constructing enantioenriched tertiary stereocenters. Analogous reactions that lead to crowded tetrasubstituted carbon centers are unknown.

To solve these problem, herein, we report that a sterically encumbered chiral N-heterocyclic carbene-Ni(0) catalyst, in conjunction with an organotriflate as electrophile and Grignard/ Zinc reagent as nucleophile , promote 1,2- diarylation of diverse alkenes and 1,3-dienes. By using this method, products bearing aryl- and alkenylsubstituted tertiary and quaternary centers could be isolated in up to 95% yield, >99:1 regioisomeric ratios and up to 96% e.e.

Publication List:

Liu,C.-F.; **Luo, X.**; Wang, H.; Koh, M. J. Catalytic Regioselective Olefin Hydroarylation(alkenylation) by Sequential Carbonickelation-Hydride Transfer. *J. Am. Chem. Soc.* **2021**, 143, 9498.

Copper Catalyzed Atroposelective Synthesis of Axially Chiral Styrenes

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Abstract

Axial chirality represents a large family of chiral platforms that are widely found in numerous chiral ligands or catalysts, synthetic building blocks, and pharmaceuticals. As an important precursor for construction of centrally chiral molecules and axially chiral biaryls, atropisomeric aryl-dihydronaphthyl skeletons have been well established. In contrast, catalytic asymmetric synthesis of axially chiral styrene with non-cyclic alkene remains underdeveloped and challenging because of the low rotational barrier and more flexible framework. The ready availability of substrates renders alkyne hydrofunctionalization an attractive strategy to address such synthetic challenges. Herein, we try to develop an atroposelective hydrophosphonylation reaction of internal alkynes to access phosphine-containing axially chiral styrenes.

Publication List

None

Asymmetric Oxo-Hydroarylation of Alkynes for Efficient Synthesis of Diarylmethanes via Photo-Driven Chiral Phosphoric Acid Catalysis

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Abstract

Alkynes represent a family of pivotal and sustainable feedstocks for various industries such as pharmaceuticals, agrochemicals and materials, and they are widely used as important starting materials for the production of a broad range of chemical entities. Nevertheless, efficient structural elaborations of alkynes in chemical synthesis, especially asymmetric functionalization of alkynes, remain largely unexplored. It is thus imperative to develop new asymmetric synthetic approaches, making use of these richly available chemical feedstocks, and enabling their conversion to value-added chiral molecules. Herein, we disclose our findings on highly enantioselective oxo-hydroarylation of alkynes, by merging photocatalysis and chiral phosphoric acid catalysis. Our reported synthetic protocol is applicable to all types of alkyne substrates, affording optically enriched diarylmethanes, important structural scaffolds in medicinal chemistry and biological sciences.

Publication List

1. Huang, Q.#; Chen, Y.#; **Zhou, X.**; Dai, L.; Lu, Y.*, Nickel-Hydride-Catalyzed Diastereo- and Enantioselective Hydroalkylation of Cyclopropenes. *Angew. Chem. Int. Ed.* **2022**, *61*, e202210560

2. Guo, J.; Shen, Z.; **Zhou, X.**; Dai, L.*; Lu, Y.* Light-induced phosphine-catalyzed asymmetric functionalization of benzylic C-H bonds. *Science China Chemistry* **2023**, *doi:10.1007/s11426-022-1406-y.*

3. **Zhou, X.**; Dai, L.*; Lu, Y.* Asymmetric Oxo-Hydroarylation of Unactivated Alkynes for Efficient Synthesis of Diarylmethanes via Photo-Driven Chiral Phosphoric Acid Catalysis. *Manuscript in preparation.*

Phosphine-Catalyzed Ring-Opening of Azetidines via C-N Bond Activation

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Abstract

Four-membered N-heterocycle azetidines are valuable building blocks in organic synthesis and are omnipresent in various natural products such as Azelnidipine and Cobimetinib. As such, synthetic methodologies to access and functionalize these useful scaffolds are highly desired and sought after by medicinal chemists. Despite the inherent ring strain (~ 25.4 kcal mol^{-1}) present in these heterocycles, the reactivity of azetidines feature a combination of unique stability and reactivity that makes modification of this moiety a challenging task. To date, common ring-opening strategies mainly rely on activating the nitrogen atom of the azetidine moiety via the use of Brønsted acids or Lewis acids. Herein, we envisioned the use of a phosphine catalyst to open azetidines via a temporarily C-N bond cleavage to form a zwitterion intermediate. Subsequently, the anionic nitrogen of this zwitterion species can then be trapped with external electrophiles to enable larger ring formation via intermolecular reactions (i.e., Michael addition).

Publication List

None

Photo-Induced Direct Alkylidenation of C-H Bonds and C-C Bond

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Department of Chemistry, Faculty of Science, National University of Singapore, Singapore

Abstract

Alkenes are a very important class of organic molecules which widely exist in natural products, bioactive molecules, and organic synthetic intermediates. Many methods for preparation of alkenes have been developed, including stoichiometric reactions of carbonyl compounds, such as the Julia-Kocienski reaction, Wittig reaction, and transition-metal-catalyzed reactions, such as Lindlar reduction, Heck reactions and olefin metathesis. In the former, equivalent sulfone compounds or phosphorus compounds are required, generating stoichiometric amounts of waste. In the latter, precious metal catalysts are required, and the substrate is limited to unsaturated compounds. Therefore, it will be revolutional to develop efficient and green catalytic methods for the direct synthesis of olefins from native substrates, such as simple alkanes and carboxylic acids.

Herein, we describe a photo-induced direct alkylidenation that uses vinyl ketone as a general alkylidenation reagent to access alkenes from abundant molecules that contain C-H bonds and carboxylic acids. The transformation reported here proceeds under milder conditions, tolerates a wide range of functional groups. Key to the success of this formal method is a C-C bond formation via radical addition process, followed by C-C bond cleavage via Norrish-type II fragmentation.

Publication List

None

Transition Metal Catalyzed Asymmetric Hydroboration of Internal Alkenes

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Abstract

Chiral organoborates are a very important class of compounds. For example, chiral boron-containing compounds are the building blocks of some drug molecules and bioactive molecules, and some chiral borides are efficient chiral catalysts. Metal-catalyzed asymmetric borohydration of olefins is one of the most effective methods for constructing chiral borates, which has attracted extensive attention from chemists because of its simple and easy availability of raw materials, high atomic economy, and diverse boronization product structures. Compared with terminal olefins like styrene, there are relatively few studies on borohydrogenation of endoolefins, especially inactivated endoolefins. This is due to the large steric hindrance of endoolefins and the difficulty of controlling the regional selectivity on both sides of the olefin. Therefore, the asymmetric borohydration of endoolefins, especially non-activated endoolefins, is quite challenging. Herein, I will introduce a series of transition metal catalyzed enantioselective hydroboration of internal alkenes including strained internal alkene, β-substituted styrenes and internal alkenes bearing a coordinating group. Additionally, we are looking for a trisubstituted or tetrasubstituted olefin to achieve asymmetric borohydration of endoolefins.

Publication List

None

Construction of P-Stereogenic Center through Long-Range Recognition

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Department of Chemistry, Faculty of Science, National University of Singapore, Singapore

Abstract

Remote asymmetric induction is one of the most challenging problems for enantioselective catalysis as the interaction between substrate and catalyst would become weaker with longer distances.[1] Most of the work on remote asymmetric induction are concentrated on forming stereogenic centers which are usually four bonds away from the site of bond formation on the meta-position of the aryl ring.[2-4] To the best of our knowledge, only an example of a specific substrate backbone using peptides catalyst for long-range recognition in the construction of stereogenic center that is located remotely to the reaction site (> 5 bonds apart) has been reported.5 Herein, we report the construction of P- stereogenic center through long-range recognition of the para-position.

Publication list

None

Chiral Acid-Catalyzed Atroposelective Indolization Enables Access to 1,1’-Indole-Pyrroles and Bisindoles Bearing a Chiral N-N Axis

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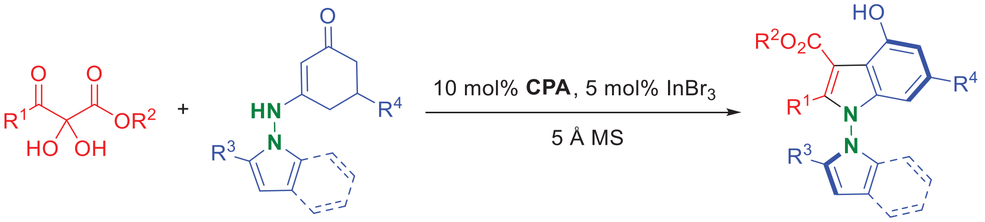
Email: e0427373@u.nus.edu

Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, China

Department of Chemistry, Faculty of Science, National University of Singapore, Singapore

Abstract



up to 92% yield, up to 94% ee

- ◆ ***Atroposelective indolization to access novel biheteroaryls with a chiral N-N Axis***
- ◆ ***Cooperative catalysis of chiral phosphoric acid and $InBr_3$ for efficient catalysis***

We present a highly atroposelective indolization for the efficient synthesis of 1,1’-biheteroaryls bearing a chiral N-N axis. Under the cooperative catalysis of chiral phosphoric acid and InBr3, the reactions between 2,3-diketoesters and 1,3-dione-derived enamines resulted in a highly enantioselective construction of 1,1’-pyrrole-indoles with up to 92% yield, 94% ee or bisindoles in up to 92% ee. Derivatizations of these compounds to diverse functionalized N-N linked axially chiral biheteroaryls have also been demonstrated.

Publication List

None

Palladium-Catalyzed Cycloaddition Using 8-Azahptafulvenes

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Department of Chemistry, Faculty of Science, National University of Singapore, Singapore

Abstract

As an important class of non-benzenoid aromatic compound, tropone is found to be the common structural motif in a large family of natural products possessing a highly varied biological activity, including antitumor, antibiotic, antibacterial and inhibitory activity. Considering the abundant pharmacological relevance of tropone and its derivatives, efficient and economical transformations of tropone analogous have been extensively

studied in the field of organic and medicinal chemistry. Palladium-catalyzed formal cycloaddition provides a simple methodology for the modification of tropone skeletons. Herein, 8-azaheptafulvenes was used to react with γ-methylidene-δ-valerolactones under palladium catalytic system. The bicyclo[5.5.0]dodecatrienes was formed by an unprecedented [8+4] higher-order cycloaddition.

Publication List

None

Enantioselective Synthesis of 2,2-Disubstituted Tetrahydrofurans and Tetrahydropyrans via Pd-catalyzed Intramolecular Allylic Substitution

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Abstract

The construction of chiral 2,2-disubstituted tetrahydrofurans and tetrahydropyrans is attractive as they are widely existed in bioactive materials. Successful protocols mainly involve [3+2] and [4+1] intermolecular cyclization, and intramolecular cyclization of olefins. Here, we report a Pd-catalyzed asymmetric allylic intramolecular cyclization of tetra-substituted terminal allylic alcohols to afford 2,2-disubstituted tetrahydrofurans and tetrahydropyrans. The reaction condition is moderate and energy-saving. Besides, the terminal allylic group of the product is easy to derivate. The highest ee so far is 95 %.

Publication List

None

Workshop Schedule

Center 2: Functional materials				
Symposium Chair: Zhang Bihan & Lin Hongbin & Yang Zhucheng				
2023/01/07				
		Presenter	**Title**	**Supervisor**
	Session Chair: Zhang Bihan			
	9:00-9:15	Zhao Junyi	Polymer-induced Synthesis of Ultra large Covalent Organic Framework Nanosheets for effective membrane desalination	Jiang Zhongyi
	9:15-9:30	Zhang Zixuan	Cationic Covalent Organic Framework Engineered Polyurea Nanofiltration Membrane for Efficient Li+/Mg2+ Separation	Jiang Zhongyi
	9:30-9:45	Gong Xiaoting	Design and synthesis nanoparticles with AIE feature for transparent mouse lung vascular imaging	Liu Bin
	9:45-10:00	Cheng Wei	In situ synthesis of copper sulfide for photothermal/chemodynamic/gas therapy	Liu Bin
	10:00-10:15	Lin Yingzheng	Metal exchange drive the generation of hollow icosahedral kernel from nonhollow icosahedral kernel in metal nanoclusters	Xie Jianping
	10:15-10:30	Liu Zhihe	Ligand Effect on Switching the Rate-Determining Step of Water Oxidation in Atomically Precise Metal Nanoclusters	Xie Jianping
	Break 10:30-10:45			
	Session Chair: Lin Hongbin			
	10:45-11:00	Zhang Bihan	A Deep Understanding on the Interactions between Gold Nanoclusters and Proteins	Xie Jianping
	11:00-11:15	Liu Zhuang	Metal halide Perovskite Nanocrystal Superlattice: Self-Assembly and Optical Fingerprints	Liu Xiaogang
	11:15-11:30	Zhao He	Flexible perovskite X-ray Detectors through perylene diimide interfacial modification	Liu Xiaogang
	11:30-11:45	Ma Yuhan	Three-dimensional hexagonal boron nitride synthesized by salt-glucose assist strategy and its application in polymer-based solid-state electrolytes	He Chunnian & Andrew Barnabas Wong
	11:45-12:00	Zhang Hanwen	In Situ Strain Induced Phase Transition and Defects Engineering in CVD Synthesized Atomically Thin MoS2	He Chunnian & Sow Chorng Haur

	Session Chair: Lin Hongbin			
	14:00-14:15	Yan Zhicheng	MOF-based material for electrocatalytic application	He Chunnian & Loh Kian Ping
	14:15-14:30	Deng Hao	Machine Learning Guided Polyamide Membrane with Exceptional Solute-Solute Selectivity and Permeance	Jiang Zhongyi & Zhang Sui
	14:30-14:45	Lyu Bohui	Molecular design of covalent-organic framework membranes for Li+/Mg2+ separation: Significant charge effect	Jiang Zhongyi & Jiang Jianwen
	14:45-15:00	Shan Huiting	Atomically Precise Gold Nanoclusters as Enzyme Mimics	Jiang Zhongyi & Xie Jianping
	15:00-15:15	Cao Lei	PDT-triggered Controllable Carbon Monoxide Therapy and Synergistic Anti-inflammation	Liu Bin
	15:15-15:30	Liu Shitai	In-Situ Synthesized Polymer Photosensitizers for Cancer-Cell-Activated Photodynamic Therapy	Liu Bin
	Break 15:30-15:45			
	Session Chair: Yang Zhucheng			
	15:45-16:00	Wang Tongtong	Organic Emitters for Device and Biological Applications	Liu Bin
	16:00-16:15	Liu Xianglong	Rational Design of Luminogens for Bacteria Imaging and Killing	Liu Bin
	16:15-16:30	Mu Chuan	Ligand-mediated Electrocatalytic Oxygen Reduction Reaction on Au25 Nanocluster	Xie Jianping
	16:30-16:45	Lin Hongbin	Engineering Electronic and Surface Structures of Metal Nanoclusters to Enhance Cluster Luminescence	Xie Jianping

Center 2: Functional materials				
Symposium Chair: Zhang Bihan & Lin Hongbin & Yang Zhucheng				
2023/01/08				
		Presenter	**Title**	**Supervisor**
	Session Chair: Yang Zhucheng			
	9:00-9:15	Liu Sirui	Adiabatic pumping of edge states in 1D non-Hermitian systems	Liu Xiaogang& Gong Jiangbin
	9:15-9:30	Jiang Zhengzhi	Quantum applications with solid-state spin defects	Liu Xiaogang
	9:30-9:45	Qiu Jian	Tin Perovskite Single Crystal Growth Assisted by Chiral Ligands	Liu Xiaogang
	9:45-10:00	Sun Guangxin	Tuning the electronic structure of MXene-based composites for electrochemical carbon dioxide reduction	He Chunnian & Andrew Barnabas Wong
	10:00-10:15	Wang Xin	Structural Evolution of MOF-Modified Copper Oxide Materials for CO2 Electrochemical Reduction Reaction	He Chunnian & Andrew Barnabas Wong
	10:15-10:30	Pu Yunchuan	Seeding with charged COF nanosheets toward MOF membranes for efficient molecular sieving	Jiang Zhongyi & Zhao Dan
	Break 10:40-10:50			
	Session Chair: Yang Zhucheng			
	10:45-11:00	Zhang Shiyu	High-flux antifouling polyamide membranes via surface grafting of polyethyleneimine and perfluorooctanoyl chloride for ionic nanofiltration	Jiang Zhongyi & Zhang Sui
	11:00-11:15	Zhang Zhiming	Machine Learning-Enabled Prediction and Rapid Screening of Metal-Organic Frameworks for Efficient Water Harvesting	Jiang Zhongyi
	11:15-11:30	Wang Dandan	Preparation and Modification of Extracellular Vesicles Enriched with Photosensitizer for Cancer Therapy	Liu Bin
	11:30-11:45	Song Wentao	Encapsulation of Dual-Passivated Perovskite Quantum Dots for Bio-Imaging	Liu Bin
	11:45-12:00	Zhuang jiahao	Chemical Modification of Functional Bacterial Cellulose through Natural in-situ Biosynthesis	Liu Bin

	Session Chair: Lin Hongbin			
	14:00-14:15	Yang Zhucheng	Construction of Thiolate-capped Magic-size Gold Sulfide (MGS) Nanoclusters via Competing Bonding	Xie Jianping
	14:15-14:30	Lyu Jingkuan	Imposition of Colloidal Instability for Gold Nanocluster Separation and Purification	Xie Jianping
	14:30-14:45	Qian Jing	Ultrafast synthesis of gold nanoclusters by manipulating the dielectric constant of the solvent	Xie Jianping
	14:45-15:00	Sui Mingyu	DNA force sensor interrogating the mechanically sensitive ion channel Piezo1	Liu Xiaogang
	15:00-15:15	Yang Dingzhu	Wireless Flexible Magnetic Hydrogel-Based pH Sensors with Fast and Ultra- Sensitive Detection for Wearable Devices	Liu Xiaogang
	15:15-15:30	Gu Chang	Ln-doped upconversion nanoparticle as a novel fluorescence probe on chromatin remodeler protein for fluorescence correlation spectroscopy	Liu Xiaogang
	Break 15:30-15:45			
	Session Chair: Lin Hongbin			
	15:45-16:00	Wei Chaolong	Superhydrophobic Three-dimensional Structure for High Performance Carbon Dioxide Electroreduction	He Chunnian & Andrew Barnabas Wong
	16:00-16:15	Li Danning	Acid Stable and Cost Effective Anodic Materials for Electrolyzers	He Chunnian & Wang Lei
	16:15-16:30	Liu Tao	Inorganic buffer and organic buffer for the neutral OER	He Chunnian & Andrew Barnabas Wong

Polymer-induced Synthesis of Ultra large Covalent Organic Framework Nanosheets for effective membrane desalination

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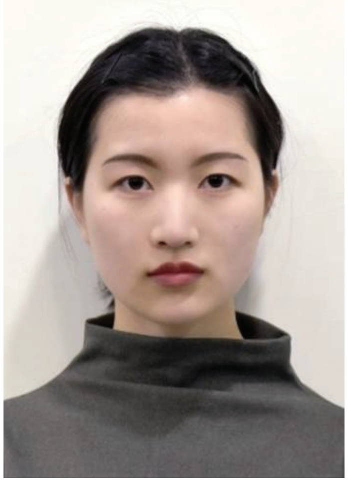
Abstract

Fresh water shortage is a global problem. Desalination is a sustainable strategy as seawater accounts for 96% of water resource globally. Compared to traditional thermal desalination, membrane technology is more energy efficient. Covalent organic frameworks (COFs) have emerged in recent years as promising materials for fast and well regulated transport, typically with COF nanosheets being the essential building blocks for their rich surface functionalities and membrane-forming ability. Achieving precise construction and regulation of the morphological structure of the COF nanosheets for effective membrane desalination process is highly desired.

In this work, inspired by the "biomineralization", we used branched polyethylenimine (PEI) to induce the formation of ultra-thin and large-size COF nanosheets, investigated the influence of PEI with different molecular weights on the morphological structure of the nanosheets, and then appliede the vacuum-assisted self-assembly method to fabricate membranes. First, we showed that PEI can induce the formation of nanosheets, and further we analyzed the role of PEI during the formation progress. Next, we changed the molecular weight of PEI and revealed its role in modulating the size and thickness of COF nanosheets, and explored the optimal COF nanosheet structure for membrane formation. Finally, we introduced one-dimensional sulfonated nanocrystal intercalation to construct hierarchical structure and assist the membrane formation process. The resulting heterogeneous COF films were tested in model seawater (3.5 wt% NaCl aqueous solution) to reveal the structure-to-performance relationship and demonstrate the potential for seawater desalination.

Publication List

Cationic Covalent Organic Framework Engineered Polyurea Nanofiltration Membrane for Efficient Li+/Mg2+ Separation



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Abstract

Attributing to the high economic value and increasing demand for lithium (Li) resources, extracting Li from salt lake brine has attracted widespread attention, the key of which is the efficient separation of Li^+/Mg^{2+}. With its green, energy-saving and high-efficiency advantages, nanofiltration (NF) is regarded as an important technology for the Li^+/Mg^{2+} separation. Covalent organic frameworks (COFs) with designable physicochemical structures and continuously distributed functional groups, are emerged as a flourishing type of nanomaterials and hold great application potential in NF. Herein, we fabricated positively charged NF membranes by embedding cationic covalent organic framework with abundant quaternary ammonium groups (COFs-DQA) into polyurea matrix to construct a selective layer for Li^+/Mg^{2+} separation. The introduction of COFs-DQA increased the membrane surface charge density to +4.13 mC m^{-2}, contributing to a stronger Donnan exclusion for Mg^{2+}, which endowed the membranes a high $MgCl_2$ rejection of 99.6% and a high Li^+/Mg^{2+} separation factor of up to 78.8.

Publication List

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

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Abstract

Visualization of vascular networks plays an important role in understanding the pathologies of lung 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.

Herein, we developed a series of AIEgens as fluorophores for transparent lung imaging, aiming at addressing the problem of fluorophores retention in different optical clearing medium. We firstly proposed a strategy to adjust the emission of AIEgens, using different “Donor and Acceptor” units, and then AIEgens form nanoparticles with amino group on the surface by self-assemble, named TSNs. Next, we combined AIEgens with tissue optical clearing technique, using TSNs-NH2 and polyacrylamide to form compact cross-linking hydrogels by covalent bonding, ensuring the stable and long-term fluorescence after continuous clearing procedures. Further, we achieved the high-resolution imaging of vascular fine structure in intact capillary-rich lung tissue by solvent-based optical clearing technique. The fluorescence of AIEgens is not quenched after continuous clearing procedures and continuous imaging acquisition for 20 min.

Publication List

1. **Gong, X.**; Hu X.; Liu J.Q.; Yang J.* and Liu B.* Aggregation-Induced Emission Nanoprobe Assisted Transparent Lung Vascular 3D-reconstruction. *Manuscript under review.*

In situ synthesis of copper sulfide for photothermal/chemodynamic/gas therapy

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Abstract

CuS has attracted considerable attention in tumor treatment due to its excellent photothermal performance. However, how to differentiate the tumor cells and cancer cells when applying photodynamic therapy is still a challenge. Some impressive works have been explored in the past years. For example, researchers deliver Cu_2O into tumor sites instead of CuS. The overexpressed H_2S of tumor cells can react with Cu_2O to form CuS, while the lower level of H_2S in normal cells cannot. However, this method is only feasible in colorectal cancer where the H_2S concentration is higher than other tumors.

In this work, we expect to develop an activable system that is applicable in all tumors. We first prepared Cu_2O coated gold nanogap. The gold nanogap can enhance the photothermal performance of CuS by virtue of LSPR effect. Then, we found a H_2S donor called diallyl trisulfide, which can generate H_2S after reacting with GSH. Afterwards, we integrate these two components into liposome. Diallyl trisulfide can be loaded into the double layer of the liposome, while Au@Cu_2O can be encapsulated in the hydrophilic core. After internalization into tumor cells, diallyl trisulfide will react with GSH to produce H_2S, which subsequently react with Au@Cu_2O to generate Au@CuS. The formed Au@CuS can be used as PTT and CDT agent under NIR light irradiation. Besides, due to the fact that the GSH level in normal cells is lower than that in tumor cells, this strategy can help to differentiate normal cells and tumor cells and selectively kill tumor cells.

Publication List

Metal exchange drive the generation of hollow icosahedral kernel from nonhollow icosahedral kernel in metal nanoclusters

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Abstract

Metal nanoclusters (NCs) with the core size smaller than 2 nm regard as the transition between single atom and nanocrystals, which show attractive molecular-like properties, such as photoluminescent, chirality. Alloying has been widely applied to custom the properties of metal NCs in term of stability, optical properties, and catalytic properties. In the alloy reaction, metal NCs with nonhollow icosahedral kernel (e.g., $Au_{25}(SR)_{28}$, $Ag_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$) are widely served as the templates for the hetero metal doping. If we could realize the originating the hollow icosahedral kernel NCs from nonhollow one through metal exchange alloy reaction, it provides a new opportunity to enrich the hollow icosahedral metal NCs family. Here, we report the generation of hollow icosahedral kernel $(AuAg)_{44}(SR)_{30}$ NCs based on the alloy reaction of nonhollow icosahedral $Au_{44}(SR)_{26}$ NCs. The step-by-step reaction was conducted to identify the key intermediates in the alloy reaction process and map out the structure evolution process. Specifically, the surface attached Cl atoms play important roles in stabilizing the structures of intermediates NCs. Moreover, as the number of Ag atoms increase, the structure of $[Au_{44-x}Ag_x(SR)_{26}]^{2-}$ (x=15-19) change to $[Au_{43-x}Ag_x(SR)_{27}]^{2-}$ (x=21-26) and finally to the hollow icosahedral kernel $[Au_{44-x}Ag_x(SR)_{30}]^{4-}$ (x=32-36). The deep understanding of the transformation process from $[Au_{44}(SR)_{26}]^{2-}$ to $[Au_{44-x}Ag_x(SR)_{30}]^{4-}$ provide a good example to generate hollow icosahedral kernel metal NCs from the broad nonhollow icosahedral kernel metal NCs library.

Publication List

1.**Lin, Y.,** Cao, Y., Yao, Q.*, Xie J.*, Revealing the composition-dependent structural evolution fundamentals of bimetallic nanoparticles through an inter-particle alloying reaction, *Chem. Sci.* **2022**, *13*, 2041.

2.**Lin, Y.,** Cao, Y., Yao, Q., O. Chai, Xie, J.*, Engineering Noble Metal Nanomaterials for Pollutant Decomposition*, Ind. Eng. Chem. Res.,* **2020***, 59,* 20561–20581.

Ligand Effect on Switching the Rate-Determining Step of Water Oxidation in Atomically Precise Metal Nanoclusters

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Abstract

The ligand effects of atomically precise metal nanoclusters (NCs) on electrocatalysis kinetics have been rarely revealed. Herein, we employ atomically precise Au_{25} NCs with different ligands (i.e., para-mercaptobenzoic acid (pMBA), 6-mercaptohexanoic acid (MHA), and homocysteine (HCys)) as paradigm electrocatalysts to demonstrate oxygen evolution reaction (OER) rate-determining step (RDS) switching through ligand engineering. $[Au_{25}(pMBA)_{18}]^-$ NCs exhibit a better performance with nearly 4 times higher than that of Au_{25} NCs capped by other two ligands. We deduce that pMBA with a stronger electron-withdrawing ability establishes more partial positive charges on Au(I) (i.e., active sites) for facilitating nucleophilic adsorption of OH^- in alkaline media. X-ray photo-electron spectroscopy (XPS) spectra and theoretical study indicate a profound electron transfer from Au(I) to pMBA in $[Au_{25}(SR)_{18}]^-$ NCs. The Tafel slope and the in-situ Raman spectroscopy suggest different ligands trigger different RDS for these Au_{25} NCs. The mechanistic insights reported here can add to the acceptance of atomically precise metal NCs as effective electrocatalysts for OER.

Publication

1. **Z Liu,** Z Wu, Q Yao, Y Cao, OJH Chai, J Xie. Correlations between the fundamentals and applications of ultrasmall metal nanoclusters: Recent advances in catalysis and biomedical applications. *Nano Today*.**2020**,36,10153.
2. O. J. H Chai#, **Z Liu#**, T Chen, J Xie. Engineering ultrasmall metal nanoclusters for photocatalytic and electrocatalytic applications. *Nanoscale*. **2019**, 11 20437.

A Deep Understanding on the Interactions between Gold Nanoclusters and Proteins

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Abstract

Gold nanoclusters (Au NCs) is the small counterpart of gold nanoparticles (Au NPs) with diameter less than 2 nm. The ultra-small size of Au NC endows them distinct molecular like properties, such as discrete electronic structures, enhanced photoluminescence and discrete redox behaviors. The ultra-small size also makes the surface of Au NCs an significant role in determining the synthesis, properties, and applications of Au NCs. The minor change of the microenvironment on the surface of Au NCs can be enlarged and reflected through the properties of Au NCs, for example, the optical properties or the catalytic reactivities of Au NCs, which is absent in its larger counterpart, Au NPs. Thus, it's rational to expect the Au NCs as promising probes to give an insight into the surface interactions between nanomaterials and exterior environment (i.e., molecules, cells, proteins, and gas.). In this work, we used the optical properties Au_{25} NCs to unveil the mechanism of the interactions between proteins and nanomaterials as the protein interactions is always a hot issue for designing nanomaterials in bio-applications. We found that the ligands on the surface of Au NCs determines the interactions with protein. The ligands with higher affinity with protein can provide stronger binding interactions and electron transfer process.

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.

Metal–halide Perovskite Nanocrystal Superlattice: Self-Assembly and Optical Fingerprints

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Abstract

Self-assembly of nanocrystals into superlattices is a fascinating process that not only changes geometric morphology, but also creates unique properties that considerably enrich the materials toolbox and give rise to new application platforms. Numerous studies have driven the blossoming of superlattices from various aspects. These include precise size and morphology control, property improvement, function exploitation, and material integration into miniature devices. The effective synthesis of metal–halide perovskite nanocrystals has boosted research on self-assembly of building blocks into micrometer-sized superlattices. More importantly, these materials exhibit abundant optical fingerprints, such as highly coherent superfluorescence, amplified spontaneous laser emission, and adjustable spectral redshift, facilitating basic research and state-of-the-art applications. This presentation summarizes recent advances in the field of metal–halide perovskite superlattices. We begin with basic packing models and introduce various stacking configurations of superlattices that form the theoretical basis for self-assembled metal–halide perovskite superlattices. We also discuss the potential of multiple capping ligands and highlight their crucial role in superlattice growth, followed by detailed reviews of synthesis and characterization methods. We then consider how these optical fingerprints can be distinguished and present contemporary applications. We conclude this presentation with a list of unanswered questions and an outlook on their potential use in quantum computing and quantum communications to stimulate further research in this area.

Publication List

1.**Liu, Z.**; Qin, X.*; Chen, Q.; Jiang, T.; Chen, Q.; Liu, X.* Metal–halide Perovskite Nanocrystal Superlattice: Self-Assembly and Optical Fingerprints. *Adv. Mater. Manuscript under review (in revision)*

2.**Liu, Z.**; Qin, X.; Chen, Q.; Chen, Q.; Jing, Y.; Zhou, Z.; Zhao, Y. S.; Chen, J.; Liu, X.* Highly Stable Lead-Free Perovskite Single Crystals with NIR Emission Beyond 1100 nm. *Adv. Optical Mater. 2022, 10, 2201254.*

3.**Liu, Z.**; Qin, X.; Liu, X.* Luminescence enrichment in perovskite-lanthanide composites: Complexity and complementarity. *Handbook on the Physics and Chemistry of Rare Earths, Elsevier, 2022, 61, 1.*

Flexible perovskite X-ray Detectors through perylene diimide interfacial modification

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Abstract

Flexible direct X-ray detectors based on perovskites show great potential for X-ray imaging due to their high sensitivity, low detection limit, low-cost and large-area fabrication. However, these detectors are still quite weak at X-ray-to-current conversion because of insufficient functional layer thickness and charge-carrier recombination. Here, we report the fabrication of a $CsPbBr_3$ quantum dot scintillators-based integrated self-powered X-ray detector comprising perylene diimide molecules embedded in the $MAPbI_3$ photoelectric conversion layer. These perylene diimide molecules can optimize crystal domain formation and carrier extraction process and two-fold increase electron mobility of $MAPbI_3$ films, thereby significantly improving X-ray detection performance. The perovskite-based integrated X-ray detector exhibits a high sensitivity of 143,169 ±848 μC Gy_{air}^{-1} cm^{-2} and a detection limit of 30.77 nGy s^{-1}. Furthermore, the flexible device demonstrated stable output against 30 severe bending cycles which can be attributed to the defect passivation and charge collection effect of the perylene diimide molecule at the grain boundary of $MAPbI_3$. These results suggest that the perylene diimide-modified integrated detector has the good potential for X-ray imaging of 3D objects with curved surface and this hybrid molecular approach provides insight into a general method to modify device performance.

Publication List

Three-dimensional hexagonal boron nitride synthesized by salt-glucose assist strategy and its application in polymer-based solid-state electrolytes

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Abstract

Hexagonal boron nitride (h-BN) with exceptional chemical and thermal stability, excellent electrical insulation properties, and high mechanical strength is promising to be used as catalyst support, interfacial protection layer toward Li metal, and enhanced additives for polymer-based electrolytes. However, powdery h-BN materials are usually fabricated in zero-, one-, and two-dimensional nanostructures based on high temperature and complex methods, which display limitations in large-scale commercial applications. Here, a novel powdery honeycomb-like h-BN with a micro-sized continuous three-dimensional (3D) structure is first established by a facile salt-glucose assist strategy at a relatively low temperature (750 °C). Meanwhile, the possible formation mechanisms of 3D structure as well as the growth approach of h-BN are put forward. As a result of structural advantages, 5 wt% 3D h-BN addition effectively improves the ionic conductivity and mechanical strength of the polyethylene oxide-based solid-state electrolyte (SSE). Therefore, this composite SSE displays enhanced electrochemical stability, realizing 126 stable cycles in the lithium symmetric cell (0.4 mA cm^{-2}) and 89 % remaining of discharge capacity (138.9 mAh g^{-1}) after 100 cycles at 1 C in the LFP//Li full cell.

Publication List

In Situ Strain Induced Phase Transition and Defects Engineering in CVD Synthesized Atomically Thin MoS2

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Abstract

Alkali metal halides have recently received great attention as additives in the chemical vapor deposition (CVD) process to promote the growth of transition metal dichalcogenides (TMDs). However, the multi-faceted role of these halide salts in modulating the properties and quality of the TMD monolayers remains mechanistically unclear. In this work, by introducing excessive gaseous NaCl into the CVD system, we demonstrate that preferential NaCl deposition along the monolayer edges causes large in situ strain that can invoke localized domains of high defect density and 2H to 1T phase transformation. HR-STEM, Raman mapping and molecular dynamic simulations revealed that higher NaCl concentrations can promote the coalescence of independent local strain domains, further increasing the 1T/2H phase ratio and defect density. Furthermore, excessive NaCl was also proven by DFT calculations to convert thermodynamic growth to kinetic growth, accounting for the unique cloud shape MoS2 crystals acquired. Compared with post-growth strain processing methods, this one-step approach for phase and defect engineering not only represents a deeper understanding of the role that NaCl plays in the CVD process, but also provides the convenient means to controllably synthesize conductive/defect-rich materials for further electrocatalysis and optoelectronic applications.

Publication List

1.Chen, B.#; **Zhang, H.#**; Liang, M.; Wang, Y.; Wu, Z.; Zhu, S.; Shi, C.; Zhao, N.; Liu, E.; Sow, C.; He, C.* NaCl-pinned antimony nanoparticles combined with ion-shuttle-induced graphitized 3D carbon to boost sodium storage. *Cell Reports Physical Science*, 3, 100891, 2022.
2.**Zhang, H.#**; Poh, E.; Sharon, L.; Zhang, Y.; Qin, H.; Xie H.; He, C. * and Sow, C.* In Situ Strain Induced Phase Transition and Defects Engineering in CVD Synthesized Atomically Thin MoS2. *Manuscript under review.*

MOF-based material for electrocatalytic application

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Abstract

High-performance electrocatalysts are key in many energy conversion systems. Presently used catalysts typically require noble metal compounds, which are costly. Furthermore, large overpotentials to drive the reaction decrease the efficiency and hinder the practical application of devices.

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

Here, we report 2DMOF and their derivatives as electrocatalysts for OER, HER, ORR and CO_2RR. Our catalysts show good electrocatalytic performances in their overpotentials, tafel slopes, electron transfer numbers, H_2O_2 yields, current densities and faradaic efficiencies. These catalytic characteristics can be utilized in the overall water splitting and zinc-air battery.

Publication List

Machine Learning Guided Polyamide Membrane with Exceptional Solute-Solute Selectivity and Permeance

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Abstract

Designing polymeric membranes with high solute-solute selectivity and permeance is important but technically challenging. Existing industrial interfacial polymerization (IP) process to fabricate polyamide-based polymeric membranes is largely empirical, which requires enormous trial-and-error experimentations to identify optimal fabrication conditions from a wide candidate space for separating a given solute pair. Herein, we developed a novel multi-task machine learning (ML) model based on an artificial neural network (ANN) with skip connections and selectivity regularization to guide the design of polyamide membranes. We used limited sets of lab-collected data to obtain satisfactory model performance over four iterations by introducing human expert experience in the online learning process. Four membranes under fabrication conditions guided by the model exceeded the present upper bound for mono/divalent ion selectivity and permeance of the polymeric membranes. Moreover, we obtained new mechanistic insights into the membrane design through feature analysis of the model. Our work demonstrates ML approach represents a paradigm shift for high-performance polymeric membranes design.

Publication List

1. **Deng, H.** #; Luo, Z. #; Imbrogno, J.; Swenson, M.T.; Jiang, Z.*; Wang, X.*; Zhang, S.* Machine Learning Guided Polyamide Membrane with Exceptional Solute-Solute Selectivity and Permeance. *Environ. Sci. Technol.* **2022**, *Just accepted*.

Molecular design of covalent organic framework membranes for Li+/Mg2+ separation: Significant charge effect

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Abstract

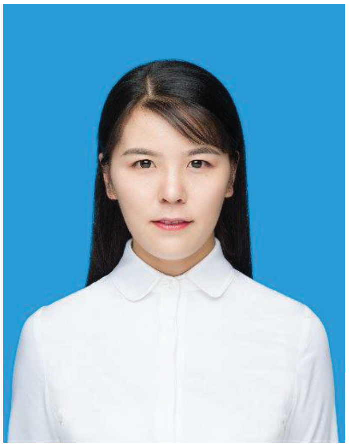
In this study, molecular simulation is utilized to explore the charge effect in COF membranes on separation performance. Three types of COF membranes with different functional groups (Tp-Tta-COOH, Tp-Tta-COO and Tp-Tta-NH_3^+) and thus different charges are designed. It is found that the positively charged membrane (Tp-Tta-NH_3^+) shows higher ion selectivity in mixed Li^+/Mg^{2+} ion solution, compared with the negatively charged and neutral membranes. In Tp-Tta-NH_3^+, the effective pore size is reduced by the secondary confinement effect of Cl ions. The orderly arranged anions (Cl) reduce the actual pore size and generate the secondary confinement effect, which fortifies the pore-entrance sieving effect, and due to the large difference in hydration energies of Li^+ and Mg^{2+} ions, the former is easier to dehydrate and enter the pore. The charge effect in Li^+/Mg^{2+} separation uncovered by molecular simulation is microscopically insightful toward the design of COF membranes and other organic framework membranes for high-performance ion separation.

Publication List

1.**Lyu, B.**; Wang, M.; Jiang, Z.*and Jiang, J.* Microscopic insight into anion conduction in covalent−organic framework membranes: A molecular simulation study. *J. Membr. Sci.* **2022**, 662, 120976

2.**Lyu, B.**; Wang, M.; Jiang, J.* and Jiang, Z.* Molecular design of covalent−organic framework membranes for Li+/Mg2+ separation: Significant charge effect. *J. Membr. Sci.* **2022**, 658, 120754

Atomically Precise Gold Nanoclusters as Enzyme Mimics



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Abstract

Natural enzymes have attracted great attention in synthetic chemistry due to their superior catalytic activity and selectivity. However, the fragile nature of natural enzymes poses a grand challenge for their broad applications in the synthesis of drugs and valuable chemicals. Therefore, there is a pressing need to explore suitable nanomaterials with robust stability as enzyme mimics. Gold nanoclusters (Au NCs) possess precise molecular formulae, tailorable functions, and well-defined inorganic-organic hybrid structures similar to natural enzymes, making them promising nanomaterials as enzyme mimics.

To verify the feasibility of gold nanoclusters (Au NCs) as enzyme mimics, atomically precise $Au_{15}(SR)_{13}$ NCs (SR = N-acetyl-L-cysteine (NAC), 3-mercaptopropionic acid (MPA), or 3-mercapto-2-methylpropanoic acid (MMPA)) are selected as the model catalysts to mimic peroxidases. Our data show that $Au_{15}(NAC)_{13}$ has a superior affinity for H_2O_2 molecules ($K_m = 3.17$), which is comparable to that of the natural enzymes. $Au_{15}(NAC)_{13}$ also exhibits high catalytic activity ($v_{max} = 0.037$ μM/s), which is about 5 times higher than that of $Au_{15}(MMPA)_{13}$. On the other hand, $Au_{15}(MPA)_{13}$ cannot be used as a peroxidase mimic due to its poor oxidation resistance. In addition, the intramolecular hydrogen-bonded peptide bond (-NH-CO-) formed by NAC endows $Au_{15}(NAC)_{13}$ with remarkable pH stability and thermal resistance. This work demonstrates the feasibility of atomically precise Au NCs as enzyme mimics and the important roles of the protecting ligands in modulating the catalytic ability and stability of Au NCs, which may provide atomic-level insights for artificial enzyme design. Based on the findings of this project, more Au NCs will be designed to reveal the rules and principles for engineering enzyme mimics with high catalytic activity and selectivity.

Publication List

PDT-triggered Controllable Carbon Monoxide Therapy and Synergistic Anti-inflammation

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Abstract

Carbon monoxide (CO) therapy has exhibited distinguished ability in various disease treatments. However, free diffusion of CO caused by inhalation leads to the risk of cytotoxicity. How to realize the controllable and on-demand release of CO gas in targeted regions remains challenging. Herein, we propose to develop photo-responsive functional nanocomposites to achieve localized CO delivery and controllable antibacterial treatment by taking advantage of oxygen-independent type-I photosensitizers. Herein, we screen out a kind of suitable type-I photosensitizers as stimulus based on the above calculations to construct a controllable CO-releasing system, which have the potential to achieve the antibacterial activity and anti-inflammation therapy.

Publication List

1. **Cao, L.** *et al*. PDT-triggered Controllable Carbon Monoxide Therapy and Synergistic Anti-inflammation. *Manuscript under review.*

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

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Abstract

Cancer is a serious threat to human health and life due to its high morbidity and mortality. For anticancer therapy, targeting and manipulating molecules that aid tumor development and growth in the tumor microenvironment can control tumor and achieve positive therapeutic results. There are many kinds of nanomaterials for tumor microenvironment response, such as liposomes, polymers, inorganic materials, and metal-organic frameworks (MOFs). Among them, MOFs are considered as a promising platform due to their porous structure and modifiability which suitable for drug carriers and reach multi-functions tailed for a specified application. Herein, we aim to develop different MOF-based nanoplatforms for anticancer therapy. For the first work, a new strategy is reported to achieve selective in-situ synthesis of polymer PSs inside cancer cells using MOF-199 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 photodynamic 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

1. Song, W.; Wang, D.; Tian, J.; Qi, G.; Wu, M.; **Liu, S.**; Wang, T.; Wang, B.; Yao, Y.; Zou, Z.; Liu, B. Encapsulation of Dual-Passivated Perovskite Quantum Dots for Bio-Imaging. *Small* **2022**, 18 (42), 2204763.

Organic Emitters for Device and Biological Applications

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Abstract

Non-invasive and real-time imaging of cells, tissues and living bodies with high temporal and spatial resolution, has shown increasing potential in biological research and clinical application. To obtain satisfactory imaging results, the emitting materials should have suitable absorption and emission wavelengths, high brightness, good photostability and biocompatibility. Based on these requirements, we chose to use tri-thiophene-based core to construct various materials with different functions. In the first work, we introduced the amine groups as recognizing units in tri-thiophene core to construct a nitric oxide probe with excellent selectivity. After reacting with nitric oxide at the site of inflammation, the probe exhibited turn-on red fluorescence immediately. The probe structure was further optimized to realize a high fluorescence turn-on ratio. In the second work, we introduced a strong electron-withdrawing unit, 1H,3H-thieno[3,4-c][1,2,5]thiadiazole, in tri-thiophene core to construct bio-imaging material with emission in the second near infrared region to detect and image tumors. In the future work, we will focus on the optimization of tri-thiophene-based imaging molecules for tumor diagnosis and therapy, hoping to further red-shift the spectrum and strengthen the phototherapeutic effect. The newly developed tri-thiophene core in this work is simple, stable, easy to synthesize and derivatize as required, indicating its great potential in developing various therapeutic agents.

Publication List

Rational Design of Luminogens for Bacteria Imaging and Killing

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Abstract

Bacterial infections diseases have been seriously threatening human health, drug resistance caused by over-range and long-term use of antibiotics also brings new challenges to clinical anti-inflammatory treatment. Constructing a multifunctional system with rapid bacterial detection and effective antibacterial effect is highly desired. Although some progress has been made in the research on PDT-based antibacterial therapy, but remains a severe challenge. In this work, we rational designed and developed a sequence of NIR light emitted luminogens with different alkyl chains, which can rapidly differentiate between bacteria and cells. This series of compounds showed strong binding ability to bacteria but not to cells. After intercalate into the bacterial membrane, the corresponding luminogens were observed complexing with nucleic acid to cause DNA aggregation, thereby effectively killing bacteria. Meanwhile, one of the presented luminogens exhibits excellent antibacterial effect against S. aureus (MIC=1 μM) and E. coli (MIC=5 μM) without harming normal cell.

Publication List

Ligand-mediated Electrocatalytic Oxygen Reduction Reaction on Au25 Nanoclusters

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Abstract

Oxygen reduction reaction (ORR) occurs at the cathode of some electrochemical systems (e.g., fuel cells) and in the Huron-Dow process, reducing oxygen to water or hydrogen peroxide. Currently, a variety of electrocatalysts have been developed to improve the efficiency of fuel cell systems or to produce hydrogen peroxide more efficiently in a green manner. However, due to the polydispersity of conventional catalysts, the relationship between catalyst structure and its electrocatalytic performance for ORR has been rarely established at the molecular or atomic level. As an emerging class of metal nanoparticles for electrocatalysis, metal nanoclusters (NCs) have atomically precise compositions and structures. In addition, the size, composition, and structure of metal NCs can be delicately tailored at the atomic level, providing a good platform to understand their structure-property correlations. Therefore, in this work we tried to adopt Au_{25} as the model electrocatalysts and use three isomers, ortho-mercaptobenzoic acid (*o*-MBA), meta-mercaptobenzoic acid (*m*-MBA) and para-mercaptobenzoic acid (*p*-MBA) as the protecting ligands to prepare $Au_{25}(MBA)_{18}$ NCs. The as-prepared $Au_{25}(MBA)_{18}$ NCs were firstly characterized by UV-vis spectroscopy and ESI-MS to make sure their high purity and monodispersity. Then RRDE system was used to determine their activities and selectivities for ORR. The results indicated that the obtained $Au_{25}(MBA)_{18}$ NCs possess really different activities and selectivities for ORR, which is most probably due to the altered electronic structure and varied catalytic micro-environment of NCs induced by the protecting ligands.

Publication List:

Engineering Electronic and Surface Structures of Metal Nanoclusters to Enhance Cluster Luminescence

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Abstract

Luminescent metal nanoclusters (MNCs) have received extensive research interest in sensing, and bioimaging due to their atomically precise size/structure and promising luminescent properties. The luminescent properties of metal NCs depend on their electronic and surface structures, which provides a good platform for designing metal NCs with desirable properties. This project will use thiolate-protected metal NCs (e.g., silver and gold) as a model to develop efficient chemical or physical processes to enhance the luminescent of metal NCs, which can be further used as a building block for designing functional devices.

In this work, we have developed an efficient physical process – mechanical force, to enhance the luminescence of silver NCs, demonstrating an interesting mechanoluminescent property. External forces can affect the core-atom stacking pattern of silver NCs, which can enhance their luminescence. We further studied the relationship between the crystallinity of metal NCs and their luminescence properties. Moreover, to further identify promising species of luminescent metal NCs, we have explored a new chemical route – the etching reactions (so-called top-down synthesis, rather than bottom-up synthesis as reported previously) to generate new luminescent species. Using Au25(MHA)18 (MHA = 6-mercaptohexanoic acid) as a model NC for the etching reaction, we have systematically studied the etching products and their corresponding luminescence properties. The etching reaction provides a good platform to generate new luminescent metal NC species. After that, one single ligand was added or removed from model NC species to realize the near infrared II region fluorescence regulation.

Publication List

1. **Lin, H.**; Wu, X.; Yao, Q.; Cao, Y.; Chen, T.; O. J. H Chai; Shan, H.; Xie, J.*; Fluorescent Enhancement of [AgS_4] Microplates by mechanical Force Induced Crystallinity Breaking. *Manuscript under review.*

2. **Lin, H.**; Cao, Y.*; Yao, Q.; Liu, Z.; Shan, H.; Chen, T.; Zhang, R.; Xie, J.*; The Synthesis of Fluorescent Nanoclusters Based on the Etching Reaction. *Manuscript under review.*
3. **Lin, H.**; Cao, Y.; Yao, Q.; Chen, T.; Xie, J.*; Revealing Etching Reaction Mechanism Based on $Au_{25}(SR)_{19}$ Nanoclusters from the Molecular Level. *Manuscript under review.*
4. Chen, T.; **Lin, H.**; Cao, Y.; Yao, Q.; Xie, J.*, Interactions of Metal Nanoclusters with Light: Fundamentals and Applications. *Adv. Mater.* **2021**, 2103918.
5. Long, S.; Feng, Y.; He, F.; Zhao, J.; **Lin, H.**; Cai, W.; Mao, C.; Chen, Y.; Gan, L.; Liu, J*.; Ye, M.*; Zeng, X.*; and Long, M.*, Biomass-derived, multifunctional and wave-layered carbon aerogels toward wearable pressure sensors, supercapacitors and triboelectric nanogenerators. Nano Energy **2021**, 105973.

Adiabatic pumping of edge states in 1Dnon-Hermitian systems

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Abstract

Recently there has been a growing interest in the study of topological properties of non-HermitianHamiltonian systems. In 1D non-Hermitian systems, topological nontrivial edge states can becharacterized by winding numbers associated to the two exceptional points. In contrast to Hermitiansystems, non-Hermitian ones can have a half-quantized winding number, which corresponds to asingle edge state localized at one edge of the system, This edge state is topologically protected by thechiral symmetry of the system. Here we find that when the chiral symmetry is broken by a mass termthe single edge state will split into two with different eigen-energies and pseudo-spin polarizationsand localize at the same edge. For a finite 1D chain, by tuning different parameters, these two edgestates can be connected to another two states localized at the other edge respectively. in an adiabatiprocess of periodic timeevolution, such a edge state will move to the other edge with a vanishingamplitude (or tends to infinity), then move back and recover the initial state with a phase factor.

Publication List

Quantum applications with solid-state spin defects

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Abstract

Spin defects in solid-state are powerful platforms for various quantum applications such as quantum computation, quantum communication, and quantum sensing. Here I first demonstrate the quantum sensing with NV center in silicon carbide. Compared with the typical spin defects, NV centers in diamond, NV center in silicon carbide works at NIR range which is more suitable for unconscious detection and preferred for bioimaging. Moreover, silicon carbide is a technology-friendly material with a large-scale production capacity and mature doping techniques, which provides opportunities to be integrated with traditional electronics. After that, I will introduce the second work where we hyperpolarize the nuclear spins in van der Waals materials via ground state level anticrossing (GSLAC) of Vb defects in hBN. We quantize the degree of nuclear spin polarization as a function of magnetic field. The magnetic field with highest nuclear polarization degree is found to be 128 mT. This work paves the first step for Vb in hBN towards a robust hyperpolarization source.

Publication List

1. **Jiang, Z.**; Cai, H.; Cernansky, R.; Liu, X.*; Gao, W.* Quantum sensing of radio-frequency signal with NV centers in SiC. *Manuscript under review.*
2. Ru, S.#; **Jiang, Z.#**; Liang, H.#; Kenny, J.; Lyu, X.; Watanabe, K.; Taniguchi, T.; Andrew, A. B.; Liu, X.; Koh, T.; Li, F.; Cai, H.; Gao, W.*. Optically induced dynamic nuclear polarization via ground state level anticrossing of color centers in hexagonal boron nitride**.** *Manuscript.*

Tin Perovskite Single Crystal Growth Assisted by Chiral Ligands

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Abstract

Compared with the reported lead-free perovskite single crystals (*e.g.* $Cs_2AgBiBr_6$, $Cs_3Bi_2I_9$, and $(NH_4)_3Bi_2I_9$), which behave reduced electronic dimensionality, 3D tin perovskite single crystals have great potential in achieving high performance environment-friendly X-ray detectors, because of their ultra-high carrier mobility. However, the huge challenges in getting large-size crystal nucleus and oriented crystal growth make it difficult to prepare high-quality 3D tin perovskite single crystals even using extra crystal seeds, resulting in the absence of X-ray detectors based on them. In this work, a new universal method about chiral ligands inducing the formation of large-size crystal nucleus and oriented crystal growth has been reported for the first time to prepare perovskite single crystals in water. Benefitting from superior anisotropy and easy-arrangement of chiral ligands (R/S)-(+/-)-α-ethylbenzylamine, the high-quality lead-free $CH_3NH_3SnBr_3$ perovskite single crystals with large size, low trap density, and enhanced stability are obtained without extra crystal seeds. Most importantly, the first tin perovskite X-ray detectors using these lead-free tin perovskite single crystals are achieved, which exhibit high sensitivity of ~2.3×10^5 $\mu C\ Gy_{air}^{-1}\ cm^{-2}$ and low detection limit of <112 $nGy\ s^{-1}$ among state-of-the-art perovskite X-ray detectors. This method about chiral ligands inducing crystal growth provides a new way for preparing high-quality bulk perovskite single crystals, and the reported tin perovskite X-ray detectors open a new family in high performance green X-ray detection.

Publication List

Tuning the electronic structure of MXene-based composites for electrochemical carbon dioxide reduction

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Abstract

Electrochemical CO2 reduction is a promising way to recycle CO2 and realize net-zero CO2 emissions. But adsorption of CO2 and further formation of *CO2 intermediate require higher energy, which limits further industrial applications. MXene is a good candidate that can adsorb CO2 and reduce the energy barrier. However, MXene materials were usually found to have HER performance, a competing reaction during ECR. Therefore, we tried to tune the electronic structure of MXene to suppress HER and enhance the ECR performance via the cations-doping method. Through the systematic investigations, we found that the MXene electronic structure can be tuned accompanying the microstructure evolutions, which are dependent on the reduction potentials of introduced cations. Additions of cations with lower reduction potential, e.g. Na+, Co2+, Ni2+, did not change the electronic structure too much, while Cu2+ and Ag+ have significant effects on its electronic structure.

Taking the in-situ reduced Ag nanoparticle decorated MXene as an example, it showed a significant improvement in ECR performance. The ratio of CO to H2 in the syngas can be tuned in the range of 1:3 to 1:1 by changing the added amount of Ag+. The result can be attributed to the change in electronic structure. With a moderate addition of cations and moderate redox reaction between MXene and cations, the electronic structure can be tuned while the MXene microstructure was kept. Therefore, with the well-kept MXene structure, the electrons can be transferred from MXene to Ag nanoparticles and the HER performance was suppressed with a suitable electronic structure. With much more addition, the MXene structure was degraded and thus blocked the electron transfer and end up with nearly 100% HER

Publication List

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Structural Evolution of MOF-Modified Copper Oxide Materials for CO_2 Electrochemical Reduction Reaction

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Abstract

With the development of industries worldwide, a huge concern has arisen on the mass release of CO_2, which contributes to the greenhouse effect and global climate change. Alternatively, CO_2 can be used as raw material to synthesize some value-added platform chemicals by electrochemical reduction reaction. In CO_2 reduction reaction (CO_2RR) systems, catalysts always play a crucial role. Recently, metal-organic frameworks (MOFs) have received increased attention to improve the CO_2RR activity because of the controllable pore size, ligand, and the open metal sites, which offer avenues to adjust the metal site environment and optimize catalytic performance. However, little is known about the actual structure of the catalytic active sites due to the dynamic restructuring of the electrocatalyst structure.

Here, copper oxide in-situ etched CuMOF materials were successfully prepared to investigate the restructuring process of surface CuMOF and find the active sites during the CO_2RR in this study. CuO@CuMOF catalysts show lower H2 evolution activity and better performance for CO_2 reduction compared with the pure CuO NS and pure HKUST-1 catalyst. It is demonstrated that some ligands (BTC) dropped off to the electrolyte, and CuMOF and CuO species in the catalyst reconstructed with reaction time. Characterization results show that CuMOF is destroyed within the first 1 min and forms coordinated HCOO-Cu complex. After that, CuO NS are reduced to Cu NS after 1 h restructure process. Finally, HCOO-Cu complex is further reduced to Cu species. This study provides new insight to understand the structural evolution of electrocatalysts during CO_2RR.

Publication List

Seeding with charged COF nanosheets toward MOF membranes for efficient molecular sieving

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Abstract

Developing ultrathin and defect-free polycrystalline metal-organic framework (MOF) membranes largely depends on seeding-induced crystallization. Here, we demonstrate a seeding strategy by employing charged, porous covalent organic framework (COF) nanosheets as nuclei-depositing substrates (NDS) to generate MOF nanosheet seeds, acquiring MOF membranes with thicknesses down to 100 nm. Based on this strategy, ultrathin ZIF-8 membranes (100-515 nm) are obtained on polymer substrate, exhibiting C3H6 permeance of 600 GPU, a C3H6/C3H8 separation factor of over 90, and superior long-term operation stability. The same strategy is extended to the fabrication of ultrathin ZIF-67 and UiO-66 membranes.

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.

High-flux antifouling polyamide membranes via surface grafting of polyethyleneimine and perfluorooctanoyl chloride for ionic nanofiltration

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Abstract

Introducing low-surface-energy fluorine materials offer great prospects for developing antifouling membranes. However, accessing fluorinated nanofiltration (NF) membranes with desirable rejection to both divalent anions and cations remains a daunting challenge. Herein, we explored fluorinated NF membranes through two-step surface modification of ultrathin polyamide membranes with polyethyleneimine (PEI) and perfluorooctanoyl chloride (PFOC) molecules successively for removing divalent ions. The existence of abundant amine groups from PEI provided positive charges for enhanced divalent cation repulsion and served as active sites for covalently grafting PEOC. The resultant membranes exhibited high rejections to both Na_2SO_4 (95.0%) and $MgCl_2$ (91.2%), combined with superior water permeance of 22.3±1.2 L m^{-2} h^{-1} bar^{-1} that outperformed the benchmark antifouling NF membranes. Moreover, the low-surface-energy perfluoroalkyl chains of PFOC render the membranes capable of combating membrane fouling caused by different foulants (flux recovery ratio>95%, total flux decay rate <15%). Our strategy may afford some valuable guidance on the rational design of advanced antifouling membranes for ionic nanofiltration.

Publication List

1.**Zhang, S.**; Shen, L.; Deng, H.; Liu, Q.; You, X.; Yuan, J.; Jiang, Z.* and Zhang, S.* Ultrathin Membranes for Separations: A New Era Driven by Advanced Nanotechnology. *Adv. Mater,* **2022**, 34, 2108457.

2.**Zhang, S.**; Zhang, R.; Li, R.; Zhang, Z.; Li, Y.; Deng, H.; Zhao, J.; Gu, T.; Long, M.; Wang, X.; Zhang, S.* and Jiang, Z.* Guanidyl-incorporated nanofiltration membranes toward superior Li+/Mg2+ selectivity under weakly alkaline environment. *J. Membr. Sci.* **2022**, 663, 121063.

Machine Learning-Enabled Prediction and Rapid Screening of Metal-Organic Frameworks for Efficient Water Harvesting

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Abstract

Atmospheric water harvesting based on metal-organic frameworks (MOFs) is a promising strategy to alleviate global water stress. Identifying MOFs with desirable water adsorption properties is keystone for the successful implementation of water harvesting. However, measuring water adsorption in MOFs by experiments is time-consuming and economically expensive. Development of efficient tools to quantify structure-property relationships and predict water adsorption performance is highly desired. In this study, we introduce a machine learning (ML) methodology to predict water adsorption properties in MOFs and screen high-performance MOFs for water harvesting. First, experimental data of water vapor adsorption isotherms in MOFs were collected, and water adsorption properties were extracted from isotherms. The quantitative structure-property relationships were analyzed, providing task-specific design principles of MOFs. Then, ML models were trained toward water adsorption properties by using both geometric and chemical descriptors. The developed ML models were applied to screen experimentally synthesized “Computation-Ready, Experimental” (CoRE) MOFs. Top-performing MOFs for water harvesting under different operating conditions were shortlisted. Moreover, the ML models were interpreted by the Gini impurity, partial dependence, and Shapley Additive Explanations. The ML-based strategy proposed in this study provides new guidelines for rational design and rapid screening of MOFs for water harvesting.

Publication List

Preparation and Modification of Extracellular Vesicles Enriched with Photosensitizer for Cancer Therapy

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Abstract

Cancer is one of the greatest threats to mankind and one in five people worldwide will develop cancer in their lifetime. Conventional cancer treatments include chemotherapy, radiotherapy, surgery and so on. Although great progress has been made on anticancer drugs and methods, complications of cancer treatment also caused huge distress to patients. Extracellular vehicles (EVs), a lipid bilayer with a diameter of approximately 40-200 nm, are promising candidates for targeting tumor cells. They possess excellent biocompatibility, enhanced permeability and retention (EPR) effect, as well as homologous targeting ability based on membrane-specific protein profiles, which makes them more favorable to be used as nanocarriers for cancer therapy. Herein, we have developed a method to modify EVs with aggregation-induced emission photosensitizers (AIE-PSs), to achieve enhanced or synergistic therapy effects for cancer therapy. AIE-PSs possess great signal-to-noise ratios and show selectively enhanced reactive oxygen species production in the aggregated state under light irradiation, offering an attractive opportunity for tracking the biogenesis of EVs and image-guided photodynamic therapy (PDT). With the assistance of AIE-PSs, AIE-EVs not only show an excellent target ability but also well PDT effect for cancer therapy.

Publication List

Encapsulation of Dual-Passivated Perovskite Quantum Dots for Bio-Imaging

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Abstract

Due to their marvelous electrical and optical properties, perovskite nanocrystals have reached remarkable landmarks in solar cells, light-emitting diodes, and photodetectors. However, the intrinsic instability of ionic perovskites, which would undergo an undesirable phase transition and decompose rapidly in ambient humidity, limits their long-term practical deployment. To address this challenge, halogenated trimethoxysilane as the passivation additive is chosen, which utilizes simultaneous halide and silica passivation to enhance the stability of perovskite nanoparticles via a dual-passivation mechanism. The processable nanoparticles show high photoluminescence quantum yield, tunable fluorescence wavelength, and excellent resistance against air and

water, highlighting great potential as green to deep-red bio-labels after further phospholipid encapsulation. This work demonstrates that the dual-passivation mechanism could be used to maintain the long-term stability of ionic crystals, which sheds light on the opportunity of halide perovskite nanoparticles for usage in a humid environment.

Publication List

1. **Song, W**.#; Wang, D.#; Tian, J.; Qi, G.; Wu, M.; Liu, S.; Wang, T.; Wang, B.; Yao, Y.; Zou, Z.; Liu, B.* Encapsulation of Dual-Passivated Perovskite Quantum Dots for Bio-Imaging. *Small* **2022**, 18, 2204763.

Chemical Modification of Functional Bacterial Cellulose through Natural in-situ Biosynthesis

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Abstract

Bacterial cellulose (BC) is a carbohydrate polymer that is widely produced by diverse bacteria with unique structural features and properties. BC has a high water-retention capacity, appealing mechanical properties, and higher purity compared to plant cellulose. Due to these attractive properties, BC has been exploited in many applications, including biomedical treatment, textiles, architecture, and environmental engineering. The functionalization methods of materials based on BC mainly focus on the chemical modification or physical coating of fermentation products, which may cause several problems, such as environment pollution, low reaction efficiency and easy loss of functional moieties during application. Thus, effective and long-lasting incorporation of functional moieties to BC remains challenging. Alternatively, biosynthetic strategies have been adopted to customize the chemical structures of BC. This approach outperforms the above-mentioned chemical modification methods in terms of being efficient and eco-friendly, which provided insights into the functionalization of BC materials through microbial modification methods. By taking the advantages of this method, we are developing functional molecules as substrate to fabricate BC with innate special properties through natural in situ bacterial metabolism.

Publication List

Construction of Thiolate-capped Magic-size Gold Sulfide (MGS) Nanoclusters via Competing Bonding

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Abstract

The robust and modifiable gold-sulfur bonding is the driving force for anchoring thiol ligands on gold surfaces, which has received great research interest in constructing multi-scale nanomaterials, especially for atomically precise nanoclusters (NCs). In sharp contrast to the extensively studied gold-thiolate (organic sulfur) protected NCs, doping gold-S2- (inorganic sulfur) into NCs is elusive and challenging. This work aims at developing hybrid sulfur-containing NCs to boost our exploration in sophisticated gold-sulfur bonding as well as the atomically precise nanoscience. In this work, a new method based on competing bonding between inorganic/organic sulfur with gold was developed to synthesize a series of thiolate-capped magic-size gold sulfide (MGS) NCs. This method also proves its versatility by successfully applying it to several other water-soluble thiol ligands (e.g., TGA, MPA, MMPA, and MHA). We then revealed the core-shell structure of MGS NCs by tandem MS (MS2) and other evidence (e.g., XPS and TEM), where the fragmentation pathways presented by MS2 clearly show the location of inorganic sulfurs. The results also exhibited a feature of homologous series for MGS NCs, among which the [Au22(SR)17S3]- (SR denotes the thiol ligand) is the dominant molecule, implying the remarkable stability endowed from this S3 core structure.

Publication List

Imposition of Colloidal Instability for Gold Nanocluster Separation and Purification

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Abstract

Separation and purification are crucial processing steps in the research and application of nanomaterials, especially for atomically precise gold nanoclusters (AuNCs). To obtain the desired AuNC from the synthesis phase while removing as much impurities as possible is always the first step before material characterization and further experiments or applications. However, currently, there is no systematic approach but trial and error for each type of AuNC. Here, we are establishing a general method for separating aqueous AuNCs protected by thiolates from the solution by merely tuning the dielectric constant and ionic strength of the solution. Electrospray Ionization Mass Spectrometry (ESIMS) shows high purity of the product after redissolution. This method is facile, safe, and effective. Moreover, it is applicable to AuNCs of different protecting ligands, such as 6-mercaptohexanoic acid (MHA), cysteine, and 4-mercaptobenzoic acid (pMBA), AuNCs synthesized using different reducing agents: $NaBH_4$, CO and glucose, and AuNCs of different sizes. A data handbook is under crafting which would act as a guideline for the separation section in the Smart Synthesis manufacturing line for AuNC that is currently under construction.

Publication List

Ultrafast synthesis of gold nanoclusters by manipulating the dielectric constant of the solvent

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Abstract

The synthesis of monodispersed gold nanoclusters (whose diameters typically are smaller than 2nm) has received great attention due to their atomically precise compositions. Although numerous methods are available for such synthesis, there are two areas for improvement. First, synthesis of gold nanoclusters is often time-consuming and typically required several days. Secondly, the separation of products and raw materials can be demanding as well. Here, we present one fast synthesis method to manufacture highly dispersed nanoclusters protected by glutathione (Au_nSG_m). In our synthesis protocol, products of gold nanoclusters are precipitated and separated easily from the reaction mixture. During the reduction growth phase, due to higher binding energy between two larger nanoclusters induced by lower dielectric constant, precipitation occurs and separates products with the other reactants. Particularly, following the same strategy, we can manipulate the size of nanoclusters by changing the dielectric constant of the solvent. More specifically, 70% ethanol can assist the formation of $Au_{25}SG_{18}$, while 50% ethanol is able to help the formation of $Au_{29}SG_{20}$. Our recipe is also applicable to other gold nanoclusters protected by different ligands, such as cysteine or lipoic acid. The wide applicability and ease of our synthetic strategy paves way for the future fast automatic production.

Publication List

DNA force sensor interrogating the mechanically sensitive ion channel Piezo1

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Abstract

The mechanically activated ion channels, Piezos play an important role in sensing touch and pressure in various cell types. There are mainly three different mechanogating models for Piezo1: the Force-from-lipids model (Piezo1 can directly sense the membrane tension), the Force-from-filament model (Piezo1 is linked with extracellular matrix or intracellular structures of the cytoskeleton and sense the force), and the membrane footprint model (Piezo's dome-shaped structure induces membrane curvature). However, the precise mechanism and structures during mechanical activation and subsequent inactivation process remain unclear. DNA structures like DNA hairpins and DNA shearing could help transmit and even measure the mechanical force in living cells which makes it possible to use the DNA structure and magnetic particles to study the activation force of Piezo1 directly. In this work, combining Micropipette and Patch clamp devices, the force-from-tether model will be further studied to find out if this model will directly contribute to the activation of Piezo1 or not.

Publication List

Wireless Flexible Magnetic Hydrogel-Based pH Sensors with Fast and Ultra- Sensitive Detection for Wearable Devices

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Abstract

Responsive hydrogels have been comprehensively studied so far and utilized in human sensing area or biomedical applications. Whereas these hydrogels like pH or temperature responsive ones, till now, are seldom exploited in commercial wearable devices, which is mainly due to the inhomogeneous and slow reactions like swelling process, relatively low strength and inconvenience and potential risks by wires and power supply. To overcome these problems, we have proposed a novel designed wireless flexible pH sensor based on magnetic pH responsive hydrogel P(HEMA-co-AA) containing NdFeB microparticles. This sensor exhibits robust, ultra-fast and sensitive responses with respect to the pH change compared with the conventional pH responsive hydrogel sensors. We innovatively combine the strong magnetic NdFeB particles with hydrogel framework. With the alteration of pH, the dependent swelling process of hydrogel will cause the deformation of the as-cast film, which will reflect a change of outer magnetic field detected further by three-dimensional Hall sensors. Particularly, we modify the film as regular micro-cylinder arrays to accelerate the swelling process by decreasing the structure feature size and meanwhile, optimize the magnetic field distribution. This work will find a new approaching for hydrogel sensor and demonstrate the responsive hydrogels applications in wearable devices like e-skin.

Publication List

Ln-doped upconversion nanoparticle as a novel fluorescence probe on chromatin remodeler protein for fluorescence correlation spectroscopy

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Abstract

Fluorescence correlation spectroscopy (FCS) provides information in dynamics of samples, most typically, the diffusion rate in 3D spacing. From which, molecular size, concentration and interaction can be interpreted. FCS measurement is composed of two parts, firstly, it directly measures the fluctuation in emission intensity of sample in a time domain, then the software generates an autocorrelation function curve (AFC) which manifests the level of 'self-correlation' of sample to itself after certain lag time. Conventional fluorescent probe used in FCS is fluorescent protein (FP), due to their excellent biocompatibility. However, most of FPs are optically excited around 480-500 nm, which will induce a strong autofluorescence by biological tissue. Addressing to the resultant low signal-to-noise ratio, we introduce lanthanide (Ln)-doped upconversion nanoparticles (UCNPs) as a new fluorescent probe for FCS, which is sensitized by 980 nm wavelength within 'tissue transparent window'. $NaYF_4$:Yb,Er@$NaYF_4$ UCNPs are bioconjugated to SWI/SNF remodeler complex, with the help of 'cell membrane breaker' peptide L17E and nuclear localization sequence (NLS), the UCNP-protein hybrid can enter human live cell nucleus, and help to monitor the chromatin remodeling process in *vitro*. The NIR excitability of UCNP is expected to reduce autofluorescence level, which is especially necessary and useful for highly-crowed nuclear environment. To the best of our knowledge, this is the first time for UCNP to be used as fluorescent probe for FCS measurement.

Publication List

Superhydrophobic Three-dimensional Structure for High Performance Carbon Dioxide Electroreduction

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Abstract

Copper-based materials are currently the most promising catalysts for CO_2 electroreduction due to the availability of high-value multi-carbon products. However, their performances are not yet suitable for large-scale applications. While efforts are focused on developing catalytic materials, it is also critical to understand and control the microenvironment around catalytic sites, which can mediate the transport of reaction species and influence reaction pathways. In this work, we report a three-dimensional superhydrophobic electrode with a stable superhydrophobic structure obtained by depositing PTFE on the bottom of copper nanoneedles (Cu NN). Benefiting from the three-dimensional structure of PTFE and Cu NN, CO_2 reduces to C_{2+} products with a high Faradaic efficiency (FE_{C2+}) of 68.4% in a H-cell and 70% in a flow cell with a current density of 350 mA cm^{-2} are achieved. These figures-of-merit are currently among the top reports within the known literature for flow cells with partial current density >200 mA cm^{-2} to C_{2+} products. Overall, this study provides a valuable strategy for designing catalysts for improved selectivity to C_{2+} products in CO_2RR.

Publication List

Acid Stable and Cost Effective Anodic Materials for Electrolyzers

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Abstract

The proton exchange membrane (PEM) water electrolysis can play an important role in hydrogen production because of its high current densities, high voltage efficiency, and compact system design. Oxygen evolution reaction (OER) at the anode is a four proton-coupled electron transfer electrochemical reaction, which is considered to dominate the overall efficiency. Currently, most catalysts for OER show poor activity and stability in an acidic environment due to the harsh reaction condition of strong oxidation imposed on the materials. Such poor activity and stability will not only hinder the application of the catalysts, but also will pose challenge to OER mechanism research. Herein, we successfully constructed a Ru-$MnCo_2O_4$ electrocatalyst, the catalyst shows a low overpotential of 210mV to reach 10mA cm^{-2} and can maintain stability within 200h in 0.5M H_2SO_4, suggesting its excellent activity and stability in acidic OER. In addition, pH-dependence experiment was also conducted to probe the OER mechanism, the results indicate that the catalyst showed similar activity in 0.5M H_2SO_4 and 1M KOH, and the results can be beneficial for revealing the change of rate determining step (RDS) during the reaction. In conclusion, this work developed a stable catalyst for acidic OER and the reaction mechanism was also carefully elucidated.

Publication List

Inorganic buffer and organic buffer for the neutral OER

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Abstract

Oxygen evolution reaction (OER) is a key half-reaction of electrochemical fuel or chemical production. Where neutral water oxidation is the most challenging limited by the local acid environments. Here, we have added a series of buffer solutions including inorganic buffer and organic buffer to alleviate the local acidification to enhance the performance. The 4 inorganic buffers and 4 organic buffers were selected as models to explore the effect and mechanism. Compared to the inorganic buffer, the organic buffer is more inclined to absorb on the surface of the catalyst, which makes some active sites invalid. The invalidation in the inorganic buffers is irreversible which is contrary to that in the organic buffers. Besides, the different catalysts show distinct feedback under the same buffer, which indicated that the interaction between these buffers and the catalysts plays an important role. In the inorganic buffers, the B-buffer showed excellent superiority to enhance neutral OER compared with the P-buffers and C-buffer. In the organic buffers, the citric buffer showed more effectiveness than the Rhodizonic-buffer.

Publication List

Workshop Schedule

7th Jan 2023: 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	Interfacial high-concentration electrolyte for stable lithium metal anode: Theory, design, and demonstration	Yang Quan-hong & Chen Wei
	9:20-9:40	Wang Lu	Bilayer separator enabling dendrite-free zinc anode with ultralong lifespan >5000 h	Yang Quan-hong & Loh Kian Ping
	9:40-10:00	Liu Yuan	In-situ photoelectron spectroscopy investigation of sulfurization-induced sodiophilic sites with model systems of α-sexithiophene and p-sexiphenyl	Chen Wei
	10:00-10:20	Luo Yani	Lithium acetylacetonate-Stabilized Oxygen Radicals towards Enhanced Cycling Stability of Li-O_2 batteries	Chen Wei
	10:20-10:40: Break			
	Session Chair: Wang Meng			
	10:40-11:00	Wang Feifei	U-Shaped Zinc Deposition with 2D MOF Nanoarrays for Dendrite-Free Zinc Batteries	Yang Quan-hong & Lu Jiong
	11:00-11:20	Da Yumin	Development of a novel Pt_3V alloy electrocatalyst for highly efficient and durable industrial hydrogen evolution reaction in acid environment	Hu Wenbin & Chen Wei
	11:20-11:40	Jin Tengyu	Electrically Tunable Two-Dimensional Homojunctions for Self-Powered Photodetection	Chen Wei

Lunch Break				
		Presenter	**Title**	**Supervisor**
Session Chair: Wang Meng				
Afternoon	14:00-14:20	Yang Haotian	Quasi-Solid-State Lithiation of Sulfur Encapsulated in Micropores	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	Directional Solidification-Induced $(110)_{Li}$ facet-Dominated Li anode for a Stable Li/Garnet Interface in Lithium Metal Batteries	Chen Wei
	15:00-15:20	Wang Meng	Facet-Controlled Bifunctional WO_3 Photocathodes for High-Performance Photo-assisted $Li-O_2$ Battery	Chen Wei
	15:20-15:40: Break			
	Session Chair: Yang Haotian			
	15:40-16:00	Cui Baihua	Design of Active and Stable Ru-based Catalysts for Hydrogen Evolution Reaction	Hu Wenbin & Chen Yanan & Chen Wei
	16:00-16:20	Zuo Yong	Customizable wrinkled hydrogels induced by salting-out effect	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
8th Jan 2023: NUS-TJU PhD Workshop				
Center 3: Energy Storage and Electrocatalysis				
Symposium Chair: Chen Wei				

		Presenter	Title	Supervisor
Session Chair: Yang Haotian				
Morning	9:00-9:20	Long Yu	Interface-engineered MXene with regulated redox activities towards enhanced ion storage	Yang Quan-hong & Chen Wei
	9:20-9:40	Zhang Weiqi	Gel Electrolyte for Low-temperature Zinc-air Battery	Liu Xiaogang & Hu Wenbin
	9:40-10:00	Wu Zhitan	Ultra-high-rate Electro-reduction of Carbon Monoxide to Carbohydrate through Intermediate Transfer in Cu-Ag Catalysts	Yang Quan-hong & Loh Kian Ping
	10:00-10:20	Cui Jiarui	Preparation of bimetallic Ni-Co-based multi-level structure electrode and its electrocatalytic performance for HER	Wang Lei & Hu Wenbin
	10:20-10:40: Break			
	Session Chair: Yang Haotian			
	10:40-11:00	Chi Jiawei	High Performance CO_2 Reduction Reaction of Copper-based Catalysts Synthesized by Thermal Shock Method	Wang Lei & Hu Wenbin
	11:00-11:20	Xiao Yukun	Multi-shells Copper Catalyst for Efficient CO_2 Reduction Reaction	Wang Lei & Chen Wei
	11:20-11:40	Chen Jie	Mechanistic studies on C–C coupling process on Cu (001) surface with fixed potential method	Chen Wei
	11:40-12:00	Ding Yishui	Investigation of Small Gas Molecules Activation Mechanism on In_2O_3(111) Surface by in-situ NAP-XPS	Chen Wei
	12:00-12:20	Meng Rongwei	Facet-modulated single-atom Pd/CeO_2 catalyst for Suzuki–Miyaura coupling	Yang Quan-hong & Lu Jiong
	12:20-12:40	Fu Xingjie	Ni-based Single Atom Catalysts In C-C coupling reactions (Suzuki-Miyaura coupling reations)	Yang Quan-hong & Lu Jiong

Interfacial high-concentration electrolyte for stable lithium metal anode: Theory, design, and demonstration

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Abstract

Lithium metal anodes hold great potential for high-energy-density secondary batteries. However, the uncontrollable lithium dendrite growth causes poor cycling efficiency and severe safety concerns, hindering lithium metal anode from practical application. Electrolyte components play important roles in suppressing lithium dendrite growth and improving the electrochemical performance of long-life lithium metal anode, and it is still challenging to effectively compromise the advantages of the conventional electrolyte (1 mol L^{-1} salts) and high-concentration electrolyte (> 3 mol L^{-1} salts) for the optimizing electrochemical performance. Herein, we propose and design an interfacial high-concentration electrolyte induced by the nitrogen- and oxygen-doped carbon nanosheets (NO-CNS) for stable Li metal anodes. The NO-CNS with abundant surface negative charges not only creates an interfacial high-concentration of lithium ions near the electrode surface to promote chargetransfer kinetics but also enables a high ionic conductivity in the bulk electrolyte to improve ionic mass-transfer. Benefitting from the interfacial high-concentration electrolyte, the NO-CNS@Ni foam host presents outstanding electrochemical cycling performances over 600 cycles at 1 mA cm^{-2} and an improved cycling lifespan of 1,500 h for symmetric cells.

Publication List

1. **Lu, H.**, Yang, C.*, Chen, W., Yang, Q.-H.*, et al. Interfacial high-concentration electrolyte for stable lithium metal anode: Theory, design, and demonstration. *Nano Res.* 2022, doi: 10.1007/s12274-022-5018-7.
2. Wang, F.#, **Lu, H.#**, Yang, C.*, Lu, J., Kang, F., Yang, Q.-H.*, et al. Demonstrating U-shaped zinc deposition with 2D metal-organic framework nanoarrays for dendrite-free zinc batteries. *Energy Storage Mater.* 2022, 50, 641-647.
3. **Lu, H.**, Yang, C.*, Chen, W.*, Yang, Q.-H.*, et al. A heat-responsive and heat-resistive separator for safe lithium batteries. *Manuscript under review.*

Bilayer separator enabling dendrite-free zinc anode with ultralong lifespan >5000 h

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Abstract

Aqueous zinc (Zn) batteries with Zn metal anodes are promising clean energy storage devices with intrinsic safety and low cost. However, Zn dendrite growth severely restricts the use of Zn anodes. To effectively suppress Zn dendrite growth, we propose a bilayer separator consisting of commercial butter paper and glass fiber membrane. The dense cellulose-based butter paper (BP) with low zincophilicity and high mechanical properties prevents the pore-filling behavior of deposited Zn and related separator piercing, effectively suppressing the Zn dendrite growth. As a result, the bilayer separators endow the Zn||Zn symmetrical batteries with a superlong cycling life of Zn anodes (over 5000 h) at 0.5 mA cm^{-2} and the full batteries enhanced capacity retention, demonstrating the advancement of the bilayer separator to afford excellent cyclability of aqueous metal batteries.

Publication List

1. Wang, L. #, Wang, F. #, Ding, Z., Liu, Y., Zhang, Z., Yang, C., Loh, K.P., and Yang, Q.-H. Bilayer separator enabling dendrite-free zinc anode with ultralong lifespan >5000 h. Green Energy Environ. 2022 (DOI:10.1016/j.gee.2022.09.013)
2. Wang, L. #, Wang Z., Li H., Han, D., Li, X., Wang. F., Gao J., Geng C., Zhang Z., Cui C., Weng Z., Yang, C., Loh, K.P., and Yang, Q.-H. Aminosilane molecular layer enables successive capture-diffusion-deposition of ions towards reversible zinc electrochemistry. ACS Nano. 2022 (DOI:10.1021/acsnano.2c09977)

In-situ photoelectron spectroscopy investigation of sulfurization-induced sodiophilic sites with model systems of α-sexithiophene and p-sexiphenyl

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Abstract

The uncontrollable sodium dendrite growth results in poor cycling performance and severe safety issues, hindering practical applications of sodium metal batteries (SMBs). To stabilize sodium metal anodes (SMAs), various strategies have been developed including employing anode hosts and electrolyte additives to establish protective layers. Nevertheless, the understanding of interaction mechanisms between protective materials and SMAs is still limited, which is crucial for the rational design of protective materials. In this work, we investigated the interaction mechanism between sodium metal and sulfur-containing functional groups with comparative model systems of *α*-sexithiophene (6T) and *p*-sexiphenyl (6P) through *in-situ* photoelectron investigations and density functional theory (DFT) calculations. Our results show that sodium atoms tend to interact with sulfur atoms and their connected carbon atoms simultaneously as well as the aromatic carbon atoms of the end groups of 6T molecules, while no chemical interaction between Na and 6P molecules is observed. The observed sulfurization-induced sodiophilic sites can shed light on the rational design of sulfur-containing protective materials and the relevant interface engineering to stabilize SMAs.

Publication List

1. **Liu, Y.#**; Lian, X.#; Xie, Z.; Yang, J.; Ding, Y.; Chen, W.*, Probing fluorination promoted sodiophilic sites with model systems of F_{16}CuPc and CuPc. *Frontiers of Optoelectronics* **2022**, *15* (1), 1-12.
2. **Liu, Y.#**; Lian, X.; Jiang, C.; Sun, Z.; Yang, J.*; Ding, Y.; Chen, W.*, *In-situ* photoelectron spectroscopy investigation of sulfurization-induced sodiophilic sites with model systems of *α*-sexithiophene and *p*-sexiphenyl. *Manuscript under review.*

Lithium acetylacetonate-Stabilized Oxygen Radicals towards Enhanced Cycling Stability of $Li-O_2$ batteries

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Abstract

To alleviate the corrosion of lithium anode and the limited stability of dimethyl sulfoxide (DMSO) in the face of superoxide radical which can cause the decomposition of DMSO via nucleophilic attack, the synergistic effect of highly dissociated lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and highly associated lithium acetylacetonate (LiA) was found to alleviate the limitations of DMSO effectively. This is mainly achieved via forming stable A-Li+…O2- intermediate to enhance the stability of DMSO-based electrolyte and accelerating the preferentially growth of film-like Li2O2 under limited capacity. Due to the electrolyte with enhanced stability under oxygen atmosphere, The Li | Li symmetric batteries using 0.4 M LiA/1 M LiTFSI/DMSO (0.4AFD) not only exhibit smaller interfacial resistance less half of that using 1 M LiTFSI/DMSO (1FD) after 17 days, but also display longer-term cycling stability up to 500 hours (vs. ~100 hours of the 1FD group). Finally, the enhanced stability of the electrolyte and lithium anode against superoxide radicals as well as the change of Li2O2 growth mechanism conspire to the decreased charge overpotential and superior cycling performance and of Li-O2 batteries when using 0.4AFD.

Publication List

Cui, X. H.; **Luo, Y. N.**; Zhou, Yin. Dong, W.H.; Chen, W. Application of Functionalized Graphene in Li-O2 Batteries. *Nanotechnology*. 2020. https://doi.org/10.1088/1361-6528/abd1a7

U-Shaped Zinc Deposition with 2D MOF Nanoarrays for Dendrite-Free Zinc Batteries

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Abstract

Aqueous zinc (Zn) battery has shown its great promise as intrinsically safe battery technology. However, Zn batteries are still far from practical use, mainly due to Zn dendrite growth and side reactions. We propose a U-shaped deposition configuration to address the dendrite issue of Zn anode, which is achieved within a nanoarray of 2D metal-organic framework (MOF) flakes grown on the Zn anode. Rich zincophilic sites of the flakes enable uniform pre-seeding of Zn ions, followed by lateral deposition of Zn metal onto the MOF flakes and bottom-up plating from the anode surface, finally achieving a U-shaped deposition. The U-shaped deposition configuration is well demonstrated by simulation results in which the ion concentration and current distribution are regulated by the MOF arrays. This procedure combining pre-seeding and bottom-up deposition naturally eliminates the "tip effect" and inhibits Zn dendrite. Together with the ideal suppression of the hydrogen evolution reaction, the Zn metal anode features long cycling stability up to 1880 h at a current density of 5 mA cm^{-2} and extends the long lifespan to full cells. This study demonstrates a renewed understanding of controlling Zn deposition in practical batteries and paves a new avenue toward dendrite-free metal anodes.

Publication List

1. **Wang, F**.; Lu, H.; Li, H.; Li, J.; Wang, L.; Han, D.; Gao, J.; Geng, C.; Cui, C.; Zhang, Z.; Weng, Z.; Yang, C.; Lu, J.; Kang, F.; Yang, Q.-H., Demonstrating U-shaped zinc deposition with 2D metal-organic framework nanoarrays for dendrite-free zinc batteries. Energy Storage Materials 2022, 50, 641-647.
2. **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, 2 (11), 1450-1463.
3. Wang, L.; **Wang, F**. (co-first author); Ding, Z.; Liu, Y.; Zhang, Z.; Yang, C.; Yang, Q.-H., Bilayer Separator Enabling Dendrite-Free Zinc Anode with Ultralong Lifespan >5000 h. Green Energy & Environment 2022.

Development of a novel Pt_3V alloy electrocatalyst for highly efficient and durable industrial hydrogen evolution reaction in acid environment

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Abstract

Alloying platinum with early transition metals is a promising approach to optimize the adsorption behaviors of catalysts. Nevertheless, the large negative redox potential between early transition metals and Pt hinders the fabrication of such alloys. Herein, we report a strategy combining the thermal shock technique with electrochemical activation to prepare Pt_3V alloy as HER catalyst for the first time. Electrochemical tests display that the as-prepared catalyst exhibits exceptional catalytic activity and durability in 0.5 M H_2SO_4, surpassing the state-of-the-art 20 wt% Pt/C. The catalyst can maintain the activity after 100 h tests without evident decay under the current density of 500 mA/cm^2. Theoretical calculations demonstrate that the optimized hydrogen absorption and high vacancy formation energy of Pt_3V contributes to the enhanced electrocatalytic activity and stability. This work may spur future research for other Pt-based early transition metal alloy catalysts for electrocatalysis.

Publication List

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Electrically Tunable Two-Dimensional Homojunctions for Self-Powered Photodetection

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Abstract

Photodetectors play an important role in future "Internet-of-Things" information society. Two-dimensional (2D) materials-based photodetectors have attracted intense interest from both academic and industrial fields, thanks to their outstanding performances and related interesting physical, electrical, and optoelectronic phenomena. However, controlling the electronic properties of the 2D materials by incorporating impurity dopants is inherently difficult due to the limited physical space in the atomically thin lattices. Here, we report a successful reconfigurable WSe2 optoelectronic device with a simple localized floating gate structure that allows reversable electrostatic doping of the channel. Fitting the I–V curve of the lateral p-n homojunction diode formed in this way with Shockley diode equation reveals an ideality factor of 1.25 and a series resistance of 0.42 MΩ, which are beneficial for highly-efficient photodetection. Under the illumination of 525-nm laser, the diode manifests high-performance self-powered photodetection. The photocurrent depends linearly on input power, giving an almost constant responsivity (*R*) value of ~ 0.17 $A \cdot W^{-1}$, which is outstanding compared with other 2D materials based homojunction devices. A maximum EQE of ~ 51%, FF of ~ 67%, and PCE of ~ 5.62% can also be obtained for the p–n homojunction. In addition, the homojunction demonstrates a wide detection spectral range from violet (405 nm) to near-infrared region (the cutoff near 1,100 nm) and maintains high R for all the wavelengths. This work opens up a promising pathway toward high performance optoelectronics based on local electrostatic doped 2D semiconductors.

Publication List

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Quasi-Solid-State Lithiation of Sulfur Encapsulated in Micropores

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Abstract

The "solid-liquid-solid" mechanism is now the dominant conversion route in the Li-S batteries, although the shuttle effect, due to the dissolution of soluble polysulfides generated during charge and discharge, results in low Coulombic efficiency and a short lifespan. Solid phase conversion sulfur cathode is an effective strategy for eliminating soluble polysulfide and improving the cycle stability of Li-S batteries. In this work, a solid phase conversion route is proposed by confining sulfur species in micropore structures, which could eliminate the generation of lithium polysulfides. In addition, cobalt was applied in the micropore channels as a catalytic activate site to accelerate the sulfur species conversion rate. The batteries show stable cycle performance with a low capacity decay rate of 0.02% per cycle in the carbonated-based electrolyte. At a low E/S ratio of 5, the batteries also show a stable cycle performance, demonstrating great promise for constructing practical Li-S batteries.

Publication List

None

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

Directional Solidification-Induced $(110)_{Li}$ facet-Dominated Li anode for a Stable Li/Garnet Interface in Lithium Metal Batteries

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Abstract

The garnet type solid-state electrolyte (LLZO) is promising to substitute the liquid electrolyte in the lithium metal batteries. However, the unsatisfying anodic interface hinders its practical application and deserves much attention. Here, we find that Li foils undergoes a directional solidification to eliminate $(200)_{Li}$ and $(211)_{Li}$, thus exposing $(110)_{Li}$ dominantly during a rapid cooling treatment (RC, 40 ℃/s). The RC-treated Li anode with dominant $(110)_{Li}$ facet displays one third the interfacial resistance and two times the critical current density (CCD) of the Li anode treated by natural cooling (NC, 0.1 ℃/s), indicating the better interfacial contact between RC-treated Li and solid-state electrolyte. Besides, the symmetric cells of RC-treated Li|Li perform a stable cycling behavior for over 5500h at 0.05 mA/cm^2 and 4500h at 0.1 mA/cm^2, which is almost 10 folds of that in the NC-treated Li|Li. Detailed analysis demonstrates that the RC-treated Li anode exhibits a low diffusion barrier, which helps induce a uniform deposition of Li and suppress the Li dendritic growth. Our study provides a facile but efficient method to improve the interfacial contact and stability between Li anode and solid-state electrolyte.

Publication List

None

Facet-Controlled Bifunctional WO_3 Photocathodes for High-Performance Photo-assisted Li-O_2 Battery

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Abstract

Photocatalysis has been recently incorporated into Li-O_2 battery to mitigate the challenge of high overpotential. However, the structure-activity relationship between photocatalytic materials and charge-discharge mechanisms in photo-assisted Li-O_2 battery has rarely been experimentally revealed. Herein, we take facet-engineered WO_3 as prototype to investigate the formation processes of discharge products and photocatalytic reaction activities. A combination of theoretical and experimental result demonstrates that controllable transition of the generated Li_2O_2 from solution growth route to surface growth route with faster redox kinetics can be realized by increasing the exposed (002)/(020) facet ratio of WO_3 photocathodes. Furthermore, the (002) facet is revealed to possess a higher oxidation ability for Li_2O_2 decomposition, thus resulting in an ultralow polarization overpotential of 0.07 V over the (002) facet dominated WO_3 photocathode. Importantly, continuous growth of Li_2O_2 film up to ~130 nm through the surface growth mode is observed on the photocathode. In-depth studies show that a Z-type heterojunction tends to be formed between the WO_3 and formed Li_2O_2, facilitating continuous growth of the Li_2O_2 film under illumination. As a result, high discharge capacity up to 10500 mAh g^{-1} is also achieved over the (002) facet dominated WO_3 photocathode. These new discoveries break through the limitation of premature battery death caused by the surface growth route and enable high capacities and sustained photo-assisted discharge.

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Design of Active and Stable Ru-based Catalysts for Hydrogen Evolution Reaction

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Abstract

Hydrogen evolution reaction (HER) is a crucial process in electrochemical energy-related technologies, which requires active, durable and low-cost catalysts in real operation. Platinum, the most efficient catalyst for HER in acidic media, has remarkably diminished kinetics in alkaline media, owing to the sluggish water dissociation step. Thus, it is of significance to explore alternatives with high performance and low cost for HER in alkaline electrolytes. Ruthenium(Ru) is a potential candidate that possesses a similar hydrogen bonding strength, but the performance is unsatisfactory until now. Here we focus on the design of highly active and stable Ru-based electrocatalysts for HER, aiming to guide the development of water electrolysis technique at a high-current low energy cost.

Publication List

none

Customizable wrinkled hydrogels induced by salting-out effect

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Abstract

The construction of a unique surface-wrinkled hydrogel with flexible customizability and highly stretchability for a wide range of applications is desirable yet challenging. Herein, we introduce a facile, universal, effective strategy to construct wrinkled hydrogels with customizable geometric dimension and well-organized wrinkle structure. Direct immersion of a prestretched poly (vinyl alcohol) hydrogel in salt for seconds and release allow rapid establishment of a continuous through-thickness modulus gradient with salting out-induced chain entanglement, thus triggering the formation of self-wrinkling structures. Moreover, the programmable wrinkled structure could be controlled by regulating the prestretching strain, salt immersing time, and salt concentration. More importantly, this strategy could be generalizable to construct PVA hydrogel with different geometries and other hydrogels, expanding the applicability and functionality of wrinkled hydrogels. This strategy, enabling hydrogels with customizable wrinkled structure, presents a universal platform for broad applications from engineering materials to wearable electronics.

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: 46,149 h^{-1}, TON: 45,000,000), 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

Elemental two-dimensional (2D) materials exhibiting intriguing properties have great potential applications in next-generation electronics. However, controlling single-phase synthesis might be challenging due to the existence of various allotropes with comparable stability. Here, low-dimensional phosphorus (P) is used as a prototype for the understanding of the competition among a series of 0D−2D allotropes upon adsorption. With a combination of theoretical calculations and scanning tunneling microscopy, we find that the formation of P allotropes significantly depends on the bond angle, coordination number, and atomic density. As a result, P atoms tend to form black phosphorene (BP)-like chains and pentamer molecules at low atomic density and 2D buckling blue phosphorene at high density. In particular, a trigonal nanoribbon-like phase is observed with the confinement of the BP-like chains. The comprehensive understanding of the evolution of the elemental allotropes in low dimension could provide fundamental guidance for the construction of polymorphic quantum materials with novel functionalities.

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Interface-engineered MXene with regulated redox activities towards enhanced ion storage

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Abstract

Materials for batteries and supercapacitors by their rapid pseudo-capacitive charge storage. With the discovery of novel MXenes, and achievements in the interface-engineering (including the structure and interfacial chemistry), new charge storage mechanisms and functions in energy storage devices have been demonstrated. Herein, it is reported that the redox activities of MXene are closely linked to their electrochemistry, and determine their interactions with Li^+ or Na^+ ions in batteries, thus affecting the capacities for Li^+ or Na^+ storage. By controlled etching of MAX precursors in eutectic molten salts, the ratio, and the kind of surface terminations (-Cl, -O), the valence state of Ti, as well as the exposed surface area, are directly and effectively tuned. As revealed, these all reflect the changes in the redox activities of the obtained Ti_3C_2. Consequently, the fined tuned Ti_3C_2 exhibits a high Li^+-storage capacity (~350 mAh g^{-1}), and a high Na^+-storage capacity (~280 mAh g^{-1}), which are far beyond the capacities displayed by the $Ti_3C_2T_x$ (T= O, F, OH) and $Ti_3C_2Cl_2$. This study unveils that the interfacial chemistry design of MXene from the aspect of synthesis provides new opportunities for boosting electrochemical performance in energy storage.

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Gel Electrolyte for Low-temperature Zinc-air Battery

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Abstract

Battery is an important device to store electricity, and it has been widely applied in various environment. Low-temperature battery can be used in civil, research and military aspects. Besides, flexible battery is also popular due to its adaptability to different demands of shape, which is important for the development of wearable devices. But the widely used lithium batteries have some limitations such as unsatisfying capacity, complicated production and hidden dangers in usage. Recently zinc-air battery has become a research focus due to its outstanding High theoretical energy density, abundant reserve in nature and high safety. At the same time, satisfying flexible battery is urgently needed due to the popularity of wearable devices. In this work, we developed a gel electrolyte with additive for low-temperature zinc-air battery, which not only realized the application for low-temperature zinc-air battery, but also improve the battery performance in cold conditions.

Publication List

None

Ultra-high-rate Electro-reduction of Carbon Monoxide to Carbohydrate through Intermediate Transfer in Cu-Ag Catalysts

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Abstract

The electrochemical reduction of CO and H_2O to high-energy-density carbohydrates [$C_x(H_2O)_y$] is an ideal approach for storing renewable energy, manufacturing industrial chemicals, and achieving the anthropogenic carbon cycle at ambient conditions. Cu is the only pure metallic catalyst with a capability of CO electroreduction, while in its bulk form the efficiency and selectivity for [$C_x(H_2O)_y$] are far too low for practical application, which is resulted from the strong concomitant hydrogen evolution reaction in aqueous solution and high tendency to generate gaseous hydrocarbons. Hence, designing an effective catalyst with an ultra-high-rate of carbon monoxide conversion and further understanding the corresponding reaction pathway are significant but challenging. Here, we develop a bimetallic Cu-Ag catalyst featuring Cu grown on the Ag nano-branch via a wet chemical reduction. Cyclic voltammetry curve and ex-situ Raman spectra prove Ag possesses a strong CO absorption capacity in aqueous solution and can induce the surface arrangement of CO on the Cu surface. Furthermore, in-situ Raman spectra prove that CH3CO* intermediate is formed on the Ag surface and then being rapidly transferred to the Cu surface, thus enhancing the yield of [$C_x(H_2O)_y$]. The Cu-Ag catalysts exhibit a high Faradic efficiency of 62% for CO-to-$C_x(H_2O)_y$ conversion and reach a high $C_x(H_2O)_y$ partial current density of 744 mA cm^{-2}.

Publication List

None

Preparation of bimetallic Ni-Co-based multi-level structure electrode and its electrocatalytic performance for HER

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Abstract

Due to the slow HER kinetic process of H-OH bond breaking (hydrolytic dissociation) and H-H bond formation (H_2 formation), traditional bimetallic nickel-based catalysts have low catalytic activity and poor durability. Therefore, it is necessary to improve the catalytic performance of bimetallic nickel-based catalysts through the regulation of morphology and structure. In recent years, increasing interfacial disorder has been considered as an effective strategy to improve the electrocatalytic activity of water decomposition materials, and the use of interfacial engineering to design and prepare amorphous/crystal heterostructures is an important way to improve the efficiency of hydrogen evolution. In this chapter, a more efficient electrode for hydrogen evolution catalyst was designed by constructing crystal-amorphous heterogeneous structure. The controllable array structure of crystalline nickel-based sulfide was combined with amorphous high-activity nickel-cobalt phosphide structure to form an amorphous - crystalline coupling $NiCoP/Ni_3S_2$ interface structure. To analyze the relationship between the structure and performance of the catalyst, the interface structure formed by different crystalline and amorphous substances was investigated, and the relationship between different interfaces on the surface morphology and phase structure of the catalyst and the catalytic HER performance was explored, which provides theoretical support and practical approaches for the design and synthesis of such electrolytic water catalytic electrodes.

Publication List

None

High Performance CO_2 Reduction Reaction of Copper-based Catalysts Synthesized by Thermal Shock Method

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Abstract

Carbon dioxide reduction technology refers to the technology of converting concentrated carbon dioxide gas and hydrogen into different chemicals under the action of catalysts. During the CO2 reduction process, CO2 is converted into carbon monoxide, ethylene, ethanol, methane, or other valuable chemicals. However, these reactions of turning CO2 into different chemicals will compete with each other and reduce the productivity of each chemical, and if we want to raise production of one of the chemicals, the catalyst system we use is very important to the whole system. Among all the metal catalysts, Copper is the only known metal that can convert CO2 to useful hydrocarbons at appreciable level. However, copper has poor selectivity toward specific chemical product, which limits further application of copper for CO2 reduction. Copper-based bimetallic alloy is one of the promising catalysts for solving the above problem, since alloys can present multiple advantage, based on different components of the alloy. But we need the different metal components to be uniformly distributed in the alloyed material, not forming a heterostructure or locally concentrated structure. Here, we introduce high temperature shock method (HTS) for alloy catalysts synthesis for CO2 reduction. The HTS technique is based on electrical Joule heating. The whole HTS process lasts only several milliseconds. During such a short time, the reaction temperature can instantaneously reach an ultrahigh level (>3000 K) with the heating/ cooling rate of 105 K s^{-1}. This technique has been widely applied in the preparation of various functional nanomaterials, especially for applications in energy storage and conversion. The HTS method has advantage in forming nanoparticles with small size, which has better catalysis activity than particles with large size. Based on this HTS method and the copper-based alloy catalysts mentioned above, we propose catalyst synthesizing of copper-based bimetallic nanoparticles for CO2 reduction using HTS method. We intend to solve key scientific questions of low selectivity toward specific chemical of copper catalyst, and uneven distribution of alloy material with low catalysis activity and product selectivity in CO2 reduction.

Publication List

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Multi-shells Copper Catalyst for Efficient CO_2 Reduction Reaction

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Abstract

Various metal-based materials have been widely generated as CO_2 reduction catalysts, many of them show Faradaic efficiency above 95% to C_1 products with relatively high current density. On the contrary, the formation of C_2 products is still much more challenging with relatively lower faradic efficiency since it requires multi-step electrons and protons transfer pathway as well as a high energy barrier. Moreover, the reaction mechanism toward C_2 and C_{2+} products remain unclear and varies from the different catalysts. The C-C coupling step is considered as the rate-determining step for C_2 and C_{2+} products affected by adsorbed CO intermediates. Here, we introduce the new multi-shells structure into Cu nanoparticles with nanovoids. The multi-shells structure make electrocatalysts capture CO intermediates and long diffusion path length, which renders CO intermediates more chances to follow the C-C coupling step and become C_2 and C_{2+} products. The multi-shell Cu presents a remark selectivity toward C_2H_4 in 1.0 M KOH electrolyte with flow cell.

Publication List

None

Mechanistic studies on C–C coupling process on Cu (001) surface with fixed potential method

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Abstract

Copper has been the best candidate to electrocatalytically reduce the CO_2 to multi-carbon products. The reason why copper has the unique property is still elusive. *OCCO is believed to be the inevitable intermediate to C2 products. Computationally, the structures of *OCCO are still under debate: is the *OCCO C-O co-adsorbed or C-C co-adsorbed on the surface? In the study, we use state-of-the-art fixed potential method to explore the stability of *OCCO under different applied potentials on Cu (001) surface. We find that in low potential, the *OCCO (C-O) is more stable, while in high potential, the *OCCO (C-C) is more stable. The energy barrier of the coupling of *OCCO (C-C) is lower than that of *OCCO (O-C). We carefully study the process of forming the *OCCO (C-C). We find that during the C-C coupling reaction, LUMO in the initial state which is an anti-bonding for C-C bonds disappears. The projections of bonding orbitals for C-C bonds are considerable in the initial state and increases in the C-C coupling process. The bonding orbitals for C-C bonds becomes LUMO in the transition states. and possibly responsible for the unique property for copper to produce multi-carbon products.

Publication List

1. Wang M.,[‡] **Chen J.,[‡]** Tian Z. L.,[‡]* Dai W. R., Cui B.H., Cui X.H., Wang D., Xiao Y. K., Lian X., Jiang C. L., Yang H. T., Wang Y. H., Sun Z. J., Ding Y. S., Sun Y. -Y., Zhang J., Chen Wei*. Facet-Controlled Bifunctional WO_3 Photocathodes for High-Performance Photo-assisted Li-O_2 Battery. *Energy & Environmental Science*, 2023, Accepted. DOI: 10.1039/D2EE03724F.

Investigation of Small Gas Molecules Activation Mechanism on In_2O_3(111) Surface by in-situ NAP-XPS

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Abstract

In_2O_3-based catalysts have recently attracted tremendous research interest due to their high activity, selectivity, and durability for the hydrogenation of CO_2 to methanol. However, the fundamental understanding of the active sites and reaction mechanisms remains unraveled, which hinders the exploration of an optimized In_2O_3 catalyst. In this work, we probed the activation of gas molecules (H_2, CO_2, and O_2) at room temperature (RT) with fully oxidized In_2O_3(111) and partially reduced In_2O_{3-x}(111) surface by using *in-situ* near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) and ultraviolet photoemission spectroscopy (UPS). It reveals that the H_2 is adsorbed as hydroxyl groups (-OH) on the In_2O_3 surface, and the surface hydroxyl and H species are more stable on the reduced In_2O_{3-x}(111) surface leading to an irreversible downward band-bending effect. Additionally, CO_2 interacts weakly with the stoichiometric In_2O_3 but strongly adsorbs on partially reduced In_2O_{3-x} surfaces with surface carbonate (CO_3^{2-}) formation. O_2 molecules are activated and dissociated by the surface to form $O_2^{\delta-}$ and O^-, leading to an electron depletion in In_2O_3 and hence resulting in an apparent upward band-bending. This upward band-bending under the O_2 exposure is reversible on the In_2O_3(111) surface and non-fully reversible on In_2O_{3-x}(111) due to the molecular chemisorbed O_2 strongly bonded to the surface oxygen vacancies. Both CO_2 and O_2 adsorption cause clear re-oxidation of partially reduced In_2O_{3-x}. Our findings can shed light on the fundamental understanding of H_2, CO_2, and O_2 activation on the In_2O_3-based heterogeneous catalytic reactions.

Publication List

None

Facet-modulated single-atom Pd/CeO_2 catalyst for Suzuki−Miyaura coupling

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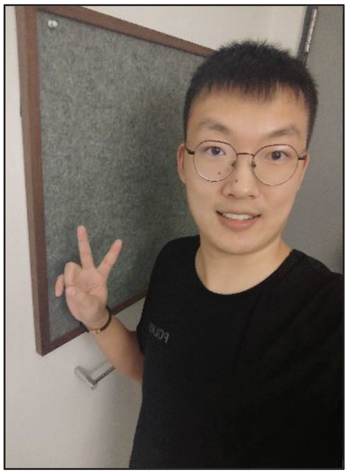
Abstract

In medicinal chemistry, the Suzuki-Miyaura cross-coupling (SMC) reaction is an attractive and useful method to achieve the coupling of carbon-carbon bonds via synthesizing asymmetric biaryl compounds. However, the existing palladium-based homogeneous catalysts are faced unavoidable problems, including high cost, toxicity and recycling difficulty. Some Pd-based heterogeneous catalysts are investigated but their catalytic activities are far inferior to that of Pd-based homogeneous catalysts. Here, we have seeded atomically Pd on CeO_2 with three different facets (100, 110 and 111, respectively) and investigate the facet effects of CeO_2 support. The coupling efficiency between aryl boronics and aryl halides catalyzed by the above three catalysts are compared. Only the Pd-CeO_2(110) catalyst shows high activity under room temperature and atmospheric pressure while Pd/CeO_2(100) and Pd/CeO_2(111) nearly cannot active SMC reaction effectively. Critical to the success are that Pd/CeO_2(110) have the highest O coordination number in the structure second shell and Pd-O-Ce(Ⅲ) catalytic center can rapidly activate reactants. This work enriches guidelines towards crystal-facet-depending activity and chemoselectivity for developing efficient synthesis methods of important industrial, agricultural and pharmaceutical intermediates or products.

Publication List

None

Ni-Based Single Atom Catalysts
In C-C coupling reactions
(Suzuki-Miyaura coupling reations)



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Abstract

Single atom catalysts (SACs), which have good activity and are inexpensive, have emerged as one of the most appealing options in the field of industrial and chemical production. Ni-based catalysts, a nonnoble catalyst, have been used for broad C-C coupling reactions. Palladium is used to catalyze the traditional Suzuki-Miyuara coupling reactions, which involve the reaction of aryl bromides, increasing the cost of manufacture. We have designed reusable SACs that catalyze the reaction, since aryl chlorides are more widely available and less expensive than other aryl halides. Our Ni-based SACs have outstanding Suzuki-Miyaura coupling reaction activity and selectivity with aryl chlorides. Over 80% of the yield of typical substrates was attained. The catalysts have a consistent catalytic performance over ten cycles and are recyclable. The performance of the Ni-based catalysts is sufficient to partially replace the Pd-based catalyst in the catalysis of the Suzuki coupling of aryl chlorides for commercial productions.

Publication List

None

Workshop Schedule

NUS-TJU PhD Online Workshop, 7th-8th Jan 2023

Center 3: Catalysis

Symposium Chair: Yan Ning

		Presenter	**Title**	**Supervisor**
Session Chair: Wang Sikai				
Jan 8th, Morning	9:00-9:20	Shi Xiangcheng	Hybrid evolutionary algorithm for global structure optimization of catalytic surface system	Gong Jinlong & Wu Jie
	9:20-9:40	Wang Wei	Surface-modified $FeVO_4$ for Chemical Looping Oxidative Dehydrogenation of Propane	Gong Jinlong & Chen Wei
	9:40-10:00	Han Xiaoyu	CO_2 hydrogenation to methanol based on $CuGaZrO_x$ solid solution	Ma Xinbin & Kawi Sibudjing
	10:00-10:20	Zheng Ying	Modifying the structure of Rh single atom to improve its catalytic performance for hydroformylation	Ma Xinbin & Yan Ning
	10:20-10:30: Break			
	Session Chair: Wang Sikai & An Hua			
	10:30-10:50	Wong Sie Shing	Effects of periodic illumination on photocatalytic amino acid production	Yan Ning
	10:50-11:10	Li Haoyue	Synthesis organonitrogen compounds using Fe_xN	Yan Ning
	11:10-11:30	Wang Sikai	H_2-reduced phosphomolybdate for room-temperature aerobic methane oxidation to methanol	Yan Ning & He Qian
	11:30-11:50	Liu Rui	Effects of scaling criteria on the packing structure and pressure drop of the packed bed using coarse grain CFD-DEM	Gong Jinlong & Yan Ning
	11:50-12:10	Wei Pingping	Tailoring bimetallic alloy catalysts for propane dehydrogenation by atomic diffusion strategy	Gong Jinlong & Yan Ning

Lunch Break				
		Presenter	**Title**	**Supervisor**
Session Chair: An Hua				
Jan 8th, Afternoon	13:30-13:50	Chang Jinquan	Electro-Thermal Water Gas Shift Reaction At Room Temperature with Pd_1/CsSMA Single Atom Catalyst	Ma Xinbin & Yan Ning
	13:50-14:10	Chen Jiyi	Developing carburized Nickel intermetallic compounds catalyst for CO2 hydrogenation to methanol	Ma Xinbin & Sibuding Kawi
	14:10-14:30	Zhou Zhaoyu	Hydrocarboxylation of Styrenes with CO2 by Sensitization-Initiated Electron Transfer	Ma Xinbin & Wu Jie
	14:30-14:50	An Hua	Demonstrating the electron-proton transfer mechanism of aqueous phase 4-nitrophenol hydrogenation using unbiased electrochemical cells	Yan Ning
	14:50-15:10	Maxim Dickieson	Creating New Generation Catalysts for CO2 Hydrogenation to Methanol	Yan Ning
	15:10-15:30	Xiao Yiying	Electrocatalytic amino acids production from biomass-derivable feedstocks over CNT	Yan Ning
	15:30-15:50: Break			
	Session Chair: Xu Di			
	15:50-16:10	Phuc T.T. Nguyen	Synthesis of chiral α-amino acids by preserving the chirality of the lignocellulosic biomass-derived substrates	Yan Ning
	16:10-16:30	Luo Ran	Role of Delocalized Electrons on the Doping Effect in Vanadia	Wang Tuo
	16:30-16:50	Zhang Yan	The effect of doping on the properties of NiO_x in perovskite solar cells	Gong Jinlong & Hou Yi
	16:50-17:10	Zhao Tianyi	Improving Computational Efficiency of Machine Learning-Based Distributed Predictive Control of Nonlinear Processes Using Feature Selection	Wang Tuo
	17:10-17:30	Hao Ziwen	Cu-based single atom pair catalysts for CO_2 hydrogenation to methanol	Sibudjing Kawi & Ma Xinbin
	17:30-17:50	Fan Ziting	Modeling of CO_2RR Using Gas Diffusion Electrode by COMSOL Multiphysics	Ma Xinbin & Lum Yanwei
	17:50-18:10	Xu Di	Non-Faradaic Promotion of Ethylene Hydrogenation under Oscillating Potentials in Fuel-cell Reactor	Yan Ning

Hybrid evolutionary 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 hybrid evolutionary algorithm (HEA) 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, HEA is especially suitable for the optimization problems that have no prior knowledge of the GMs.

Currently, we already developed a parallel, multi-population HEA 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).

Publication List

Shi X, Lin X, Luo R, et al. Dynamics of Heterogeneous Catalytic Processes at Operando Conditions[J]. JACS Au, 2021, 1(12): 2100-2120.

Surface-modified $FeVO_4$ 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, as well as experiences a growing gap between supply and demand, thereby needing a new technology to tackle this dilemma. Chemical looping oxidation dehydrogenation of propane (CL-ODHP) affords a promising platform to implement selective production of propene, whereas remains challenging. Herein, we report alkaline earth metals (Mg, Ca, Sr and Ba) as effective promoters to modify redox-active oxygen carrier with superior oxygen storage capacity, i.e., $FeVO_4$, for CL-ODHP. The unpromoted $FeVO_4$ exhibited poor propene selectivity, while addition of Mg promoter achieved up to 85% propene selectivity at 550 °C. Characterizations indicate that $MgVO_x$ species formed on $FeVO_4$ acting as active sites for C–H bond activation, which inhibit unselective CO_2 formation.

Publication List

1. Song, H.; **Wang, W. (co-first)**; Z.-J. Zhao*. Chemical looping oxidative propane dehydrogenation over $FeVO_4$ oxygen carrier pellets (In press)
2. **Wang, W.** Chen W. Gong, J*. Surface-modified $FeVO_4$ for Chemical Looping Oxidative Dehydrogenation of Propane (In preparation)

CO_2 hydrogenation to methanol based on $CuGaZrO_x$ solid solution

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Abstract

The development of a highly efficient catalyst for CO2 activation and selective conversion to methanol is critical to address the issues associated with the high thermal stability of CO2 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 a series of CuGaZrOx solid solution catalysts for CO2 hydrogenation to methanol. The size effect of Cu was studied by changing the loading of Cu was studied. The single atom Cu in the surface of catalyst showed the best catalytic performance. The synergistic effect between Cu and Ga promotes the CO2 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 CO2 hydrogenation to methanol.

Publication List

1. **X. Han**, M. Li, X. Chang, Z. Hao, J. Chen, Y. Pan, S. Kawi, X. Ma, Hollow structured Cu@ZrO_2 derived from Zr-MOF for selective hydrogenation of CO_2 to methanol, Journal of Energy Chemistry, 71 (2022) 277-287.
2. X. Chang, **X. Han**, Y. Pan, Z. Hao, J. Chen, M. Li, J. Lv, X. Ma, Insight into the Role of Cu–ZrO_2 Interaction in Methanol Synthesis from CO_2 Hydrogenation, Industrial & Engineering Chemistry Research, 61 (2022) 6872-6883.

Modifying the structure of Rh single atom to improve its catalytic performance for hydroformylation

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Abstract

Hydroformylation is an industrially important homogeneous catalytic reaction for production of aldehydes. Nowadays, phosphine ligand-containing Rh complexes are widely applied in industrial processes because of their superior catalytic activity. However, the problems of catalyst separation and recycling limit the practical production efficiency. The single-atom catalysts combine the advantages of high activity of homogeneous catalysts, with reusability of heterogeneous catalysts, and thus would be a promising alternative to the traditional homogeneous hydroformylation catalysts.

Controlling the local environment of atomically dispersed metal atoms play significant roles in determining activity and selectivity of single-atom catalysts. We tuned the local environment of Rh single atom on CeO2 via adjacent MnOx. Single atom Rh/MnOx-CeO2 exhibits more easily formation for active species of Rh+ and a lower activation energy for rate determining step, accounting for improved hydroformylation rates. This work has identified an efficient heterogeneous hydroformylation catalyst and contributes to new insight into the adjusting the intrinsic property of single-atom Rh catalysts and catalytic mechanism.

Publication List

Effects of periodic illumination on photocatalytic amino acid production

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Abstract

Despite numerous studies on controlled periodic illumination to improve the quantum yield of photocatalytic reactions, debates still exist on whether the observed enhancement is genuine as well as the nature of the enhancement effect. In addition, most studies focus on utilising a half reaction as the main process while the other half is often neglected. Here, we studied the effects of periodic illumination on photocatalytic conversion of lactic acid into alanine over commercial CdS and CdS nanosheets. We demonstrated that alanine productivity under intermittent illumination at 7 Hz with various duty cycles is similar to static illumination at equivalent light intensity. Therefore, no quantum yield enhancement was observed for this reaction under periodic illumination.

Correlation between H_2 evolution and alanine productivity over both catalysts under periodic illumination suggested that periodic illumination does not induce changes in reactive states of both catalysts since product selectivity remained unchanged regardless of mode of illumination. Kinetic modelling was then conducted and the results proposed that the rate constants for lactic acid oxidation and imine reduction increased by factors of up to 4 and 2 respectively for CdS nanosheet (up to 15 and 1.1 respectively for commercial CdS) with decreasing duty cycles. However, the ratio of reaction rate constant to recombination for lactic acid oxidation (rate determining step) is ~10^{-5}. Therefore, this result suggests that the increment in oxidation rate constant is insufficient to induce overall catalytic enhancement in photocatalytic alanine production from lactic acid, leading to the observed “light intensity effect”.

Publication List

1. **S.S. Wong**; R. Shu; J. Zhang; H. Liu*; N. Yan*; Downstream processing of lignin derived feedstock into end products. *Chem. Soc. Rev.* **2020**, 49, 5510-5560.
2. M.J. Hülsey; C.W. Lim; **S.S. Wong**; N. Yan*; Coverage-dependent formic acid oxidation reaction kinetics determined by oscillating potentials. *Mol. Catal.* **2021**, 504, 111482.

3. Y. Zhou; J. Zhang; L. Wang; X. Cui; X. Liu, **S.S. Wong**; H. An; N. Yan*; J. Xie; C. Yu; P. Zhang; Y. Du; S. Xi; L. Zheng; X. Cao; Y. Wu; Y. Wang; C. Wang; H. Wen; L. Chen; H. Xing*; J. Wang*; Self-assembled iron-containing mordenite monolith for carbon dioxide sieving. *Science* **2021**, 373, 315-320.
4. **S.S. Wong**; M.J. Hülsey; H. An; N. Yan*; Quantum yield enhancement in the photocatalytic HCOOH decomposition to H_2 under periodic illumination. *Catal. Sci. Technol.* **2022**, 12, 5217-5228.

Synthesis organonitrogen compounds using Fe_xN

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Abstract

Alkylamines and their derivatives are macroscale feedstocks in industries, and alcohols are the mainstream substrates in the alkylamines synthesis process. The most researched catalysts in amination process are Ru-, Rh-, Pd-, and Ni-based catalysts, in which the main nitrogen source is ammonia. Iron has not been studied for the amination process extensively, and the abundance and low price of iron makes it attractive. More importantly, iron is a vital metal element in nitrogen activation process, which may highlight the potential of directly activating nitrogen gas and introducing it into organic compounds. Here, iron nitride was tested for the amination of isopropanol to form isopropylamine without supplying other nitrogen source in the fixed-bed reactor. The yield of isopropylamine reached 65% initially and decreased gradually due to consumption of nitrogen in the iron nitride at 250 ℃ and 10 bar. The iron nitride was first synthesized in situ by nitridation of Fe_3O_4, and the nitrogen content was determined by the elemental analysis. Around 80% of nitrogen in the iron nitride was transferred to isopropanol for isopropylamine formation, while the other was consumed by hydrogen to form gaseous ammonia. The main reactive species, the hydrogen partial pressure effect, and the reaction pathway were investigated based on stepwise control experiments, in-situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), and X-ray spectroscopy (XPS).

Publication List

1. **Haoyue Li,** Ning Yan*. Unlocking the Potential of Photocatalysts in Biomass Refinery. *Chem*, **2020**, 6, 2871-2873.
2. Xi Chen, Song Song, **Haoyue Li,** Gökalp Gözaydın, Ning Yan*. Expanding the Boundary of Biorefinery: Organonitrogen Chemicals from Biomass. *Account of Chemical Research,* **2021**, 54, 1711-1722.

H2-reduced phosphomolybdate for room-temperature aerobic methane oxidation to methanol

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Abstract

The selective oxidation of methane with molecular oxygen to value-added chemicals, such as methanol, has aroused intense research interests during the past decade. However, due to the inert structure of methane, the process still suffers from low conversion and poor methanol selectivity, especially at room temperature.

Inspired by methane monooxygenase (MMO), a class of enzyme using in situ reduced transition metal sites for highly efficient methane oxidation under ambient conditions, we developed a Pd-containing phosphomolybdate catalyst, which, after activation by H_2, converts methane into methanol with almost 100% selectivity using O_2 at room temperature. Atomically dispersed Pd enables rapid hydrogen spillover to phosphomolybdate for Mo reduction, while facile oxygen and subsequent methane activation occurs on the reduced phosphomolybdate sites.

Additionally, we found that adding promoters to the solution or catalyst surface could effectively promote the methane oxidation performance. By adding SO_3^{2-} as the reducing agent, the methanol productivity increased by roughly 5 times without compromising methanol selectivity. Furthermore, by adopting hydrophobic molecules modification, the methanol productivity was also significantly enhanced. Possible explanations are given and more experiments are being carried out to give detailed evidence.

Publication List

1. Hülsey, M. J.; Baskaran, S.; Ding, S.; **Wang, S.**; Asakura, H.; Furukawa, S.; Xi, S.; Yu, Q.; Xu, C.-Q.; Li, J.*; and Yan, N.* Identifying Key Descriptors for the Single-Atom Catalyzed CO Oxidation, *CCS Chemistry* **2022**, 4, 3296–3308.
2. Chen, J.; **Wang, S.**; Peres, L.; Collière, V.; Philippot, K.; Lecante, P.; Chen, Y.*; Yan, N.* Oxidation of Methane to Methanol over Pd@Pt Nanoparticles under Mild Conditions in Water. *Catalysis Science & Technology* **2021**, *11,* 3493-3500.
3. **Wang, S.**; Yan, N.* X-ray Absorption Spectroscopy: An Indispensable Tool to Study Single-Atom Catalysts. *Synchrotron Radiation News* **2020**, 33, 18-26.

Effects of scaling criteria on the packing structure and pressure drop of the packed bed using coarse grain CFD-DEM

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Abstract

High fidelity 3-D numerical calculation through classical CFD-DEM approach is rather time consuming and expensive. This work employs the coarse grain approach through lumping real particles into one representative parcel to function as an accurate and efficient physical method to simulate the random packed bed. Two kinds of representative modification criteria for particle contact interaction are discussed considering the numerical accuracy of CGDEM. It has been uncovered that when the particles overlap is confined directly, according to the dimensionless value, kr/mg, a rather large spring constant should be chosen to maintain the similar particle contact area. It suggests that above criteria are only favorable for solid particle with high hardness. While when the dimensionless particles overlap is fixed, the numerical result of CGDEM is comparable to that through CFD-DEM in regardless of spring constant, indicating its much wider application field towards solid particle with various physical property. Furthermore, the uncertainty in CGDEM induced from the increase of real particle number lumped into one parcel is also discussed to promote the application in large scale industrial process. A quantitative analysis shows that the numerical error will be enhanced as parcel size increase and display no significant variation with domain size under periodic boundary. The reason responsible for above phenomenon is also uncovered. Disregarding the voidage inside parcel could affect the simulation of porosity in fixed bed and hence deviate the predicted hydrodynamics away from the CFD-DEM model. What's more, the comparison of wall time spent to simulate 1 physical second illustrates the coarse grain model solver is much faster compared with DEM approach, indicating its high simulation efficiency.

Publication List

1. **Rui Liu**, Xianhua Zhang, Tao Liu, Xian Yao, Zhijian Zhao, Chunlei Pei*, and Jinlong Gong*, Dynamic Oxygen Migration and Reaction over Ceria-Supported Nickel Oxides in Chemical Looping Partial Oxidation of Methane. *Manuscript under review.*
2. Tao Liu, Chunlei Pei, Tingting Yang, Xianhua Zhang, **Rui Liu**, Zhi-Jian Zhao, and Jinlong Gong*, Promoted Oxygen Release from Copper-ceria Interfacial Sites for Selective Hydrogen Production. *Manuscript under review.*

Tailoring bimetallic alloy catalysts for propane dehydrogenation by atomic diffusion strategy

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Abstract

Propylene is an important platform material in the chemical industry, as it’s used for producing enormous petrochemicals such as polypropylene, acrolein and so forth. With the increasing demand for propylene and abundant supply of propane from the shale gas revolution, an efficient and economical on-purpose propylene production method, propane dehydrogenation (PDH), has drawn a lot of attention in recent years. The development of the PDH method sponge on the high performance of catalysts. Nanostructured catalysts (NCs) often show distinguished catalytic performance because of tunable “geometric effect” and “electronic effect”. While NCs are constrained by thermodynamical metastability due to their high surface energy. For commercially used Pt-based catalysts, the bimetal strategy was widely applied to manipulate its geometric and electronic structure, assuring improved stability and great selectivity.

Here, we focus on the synthesis of Pt-based bimetallic nanocatalysts by atomic diffusion strategy. The catalyst surface/interface structure was rationally designed to efficiently activate propane C-H bonds and selectively produce propylene. We synthesized a series of silica-supported PtZn bimetallic catalysts. Screened catalyst shows superior catalytic performance over PDH, with a propane conversion of 59% and propylene selectivity of more than 96% at 600°C. After 10 hours of continuous testing at 600 °C, the catalyst shows favorable stability without lowering the performance. The particle size distribution of these bimetallic catalysts is mainly concentrated on the sub-nanometer scale, and the nanoparticles are uniformly distributed on the silica. Relying on the TEM analysis and CO-DRIFTS, the PtZn bimetallic alloy was distinguished. The influence mechanism of geometric and electronic effect of PtZn was also investigated.

Publication List

None

Electro-Thermal Water Gas Shift Reaction At Room Temperature with Pd_1/CsSMA Single Atom Catalyst

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Abstract

Water-gas shift (WGS) reaction is often conducted at elevated temperature and requires energy-intensive separation of H_2 from methane (CH_4), carbon dioxide (CO_2) and residual CO. Designing processes to decouple CO oxidation and H_2 production provides an alternative strategy to obtain high purity H_2 streams. Herein, we report an electro-thermal WGS process combing thermal oxidation of CO on a silicomolybdic acid (SMA)-supported Pd single-atom catalyst (Pd_1/CsSMA) and electrocatalytic hydrogen evolution. Those two half-reactions are coupled through phosphomolybdic acid (PMA) as a redox mediator at a moderate anodic potential of 0.6 V (versus Ag/AgCl). Under optimized conditions, our catalyst exhibited a TOF of 1.2 s^{-1} with turnover numbers above 40,000 mol_{CO2}/mol_{Pd} achieving stable H_2 production with a purity consistently exceeding 99.99%.

Publication List

None

Developing carburized Nickel intermetallic compounds catalyst for CO_2 hydrogenation to methanol

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Abstract

CO_2 captured and utilization technology is among the hottest topics in research due to the serious situation caused by the over-emission of CO_2 gas. Methanol, as a potential product from CO_2 hydrogenation, has attracted more people's attention than ever, because it could not only serve as an energy carrier, but also is used as a key feedstock for various chemicals in industry. In practice, traditional $Cu/ZnO/Al_2O_3$ catalyst generally suffers from the low methanol selectivity and the poor stability at high CO_2 conversion. Therefore, it is still necessary to develop better catalysts for the advancement of CO_2 to methanol technique.

Here, we designed a novel Nickel-based catalyst, carburized Nickel Indium intermetallic compounds catalyst, for CO_2 hydrogenation to methanol. Different from the typical Nickel-based catalysts and carbide catalysts which in favour of CH_4 and CO during CO_2 hydrogenation, this carburized Nickel Indium intermetallic compounds catalyst inversely shows higher selectivity for methanol. By screening synthesis protocols, we further optimized the catalytic performance, displaying 13.4% CO2 conversion and 60% methanol selectivity at 553 K, 4 MPa, which endowed the potential to this catalyst for future industrial applications.

Publication List

1. X. Han, M. Li*, X. Chang, Z. Hao, **J. Chen**, Y. Pan, S. Kawi*, X. Ma*, *J. Energy Chem*. **2022**, 71, 277.
2. X. Chang, X. Han, Y. Pan, Z. Hao, **J. Chen**, M. Li*, J. Lv, X. Ma, *Ind. Eng. Chem. Res*. **2022**, 61, 6872.
3. **J. Chen**, M. Li*, X. Han, Z. Hao, Y. Pan, H. Zhang, X. Zi, S. Kawi*, X. Ma*, Crystal Facet-dependent Effect of h-In_2O_3 Catalyst for CO_2 to Methanol. *Manuscript writing.*

Hydrocarboxylation of Styrenes with CO_2 by Sensitization-Initiated Electron Transfer

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Abstract

Carbon dioxide (CO_2) is a well-known greenhouse gas and has gained considerable attention as an ideal C1 source in chemical transformations, therefore chemists have endeavored to achieve "waste to wealth" conversion by transforming CO_2 into value-added fuels and fine chemicals. Among the chemical transformations utilizing CO2, hydrocarboxylation of styrenes with CO_2 has attracted considerable attention, representing an efficient way to generate bioactive and synthetically useful carboxylic acids. Transition metal catalysis and later photocatalysis have been explored to achieve this reaction, while excess metal or organometallic reductants must be added in transition metal catalysis and ultraviolet light is utilized to achieve *β*-selective hydrocarboxylation. Here, we have developed a scheme to achieve *β*-selective hydrocarboxylation in a short reaction time under visible light without adding any metal or organometallic reductants. Both terminal styrenes and internal styrenes (α-substituted and *β*-substituted) with variant substitutes are viable substrates under this condition. A broader substrate scope and detailed mechanism are still in progress.

Publication List

None

Demonstrating the electron-proton transfer mechanism of aqueous phase 4-nitrophenol hydrogenation using unbiased electrochemical cells

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Abstract

Heterogeneous thermocatalytic hydrogenation is widely believed to occur via co-adsorption of H2 and other reactants, but in aqueous phase an ionic or electrochemical mechanism was also proposed. Herein, we conduct 4-nitrophenol hydrogenation in an unbiased H-cell, where H2 and substrate are separately supplied into two chambers connected by a proton exchange membrane, in comparison with the same reaction in a single-cell in which H2 and 4-nitrophenol are co-fed. Based on the observation of the almost identical hydrogenation performance between the H-cell and the single cell, we conclude that co-adsorption of H2 and 4-nitrophenol is not a prerequisite for hydrogenation in aqueous phase in the tested pH range. Isotope experiments, scavenger test, DFT calculations and reaction kinetics suggest that a coupled electrochemical half-reaction mechanism for 4-nitrophenol hydrogenation in acidic aqueous phase is predominant. Importantly, while H2 oxidation primarily occurs on metal sites, 4-nitrophenol reduction occurs on both metal sites and conductive support, highlighting the non-innocent role of the support if the hydrogenation reaction follows the electron-proton transfer pathway.

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Creating New Generation Catalysts for CO_2 Hydrogenation to Methanol

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Abstract

Anthropogenic carbon dioxide (CO_2) emissions have been identified as a key component in climate change and ocean acidification—yet paradoxically—CO_2 also presents opportunity for an abundant and sustainable carbon source to produce key chemicals. In particular, CO_2-to-methanol has received extensive interest from academia and industry as a popular strategy for recycling CO_2 in efforts towards establishing a circular carbon economy. As a vital component in commercial fuels and feedstock for conversion into commodity products, global methanol production is roughly 110 Mton/year worth about $55 trillion annually, presenting a golden opportunity to replace environmentally harmful natural gas derived production routes with green, totally renewable CO_2-derived methanol. At present, the commercial $Cu/ZnO/Al_2O_3$ catalyst is employed for CO_2 hydrogenation to methanol; however, operation faces crucial obstacles related to inadequate catalyst stability under exposure to heat and moisture, causing rapid deactivation that hinders long-term process functionality. As such, the price of renewable methanol remains too high in comparison CH_4-derived methanol to be brought to market and development of more active and stable catalysts are desired to address the cost-competitiveness barrier CO_2-derived methanol currently faces.

In this proposal, I will present my physical mixing approach, integrated with a systematic study on synthesis conditions, for improving activity and/or stability of CO_2 hydrogenation to methanol catalysts. The first is based on a previously reported $ZnZrO_x$ catalyst, which has received noted attention recently due to its excellent stability, but has yet to reach the activity of $Cu/ZnO/Al_2O_3$. Several strategies such as metal promotor addition and increasing surface area have been applied to improve the activity of $ZnZrO_x$, but nonetheless, literature reports random activities that suggest an underlying structural parameter is affecting catalytic performance. In this project, we employ a systematic study on synthesis conditions to prepare ten different iterations of the $ZnZrO_x$ catalyst, each with different structural properties. The structure-activity relationships revealed surface oxygen content is a vital component for catalytic activity as $ZnZrO_x$ with higher surface oxygen content reported higher area-normalized catalytic activity. Lattice oxygen was identified as being essential for constituting active sites and is very sensitive to synthesis conditions. Unlike conventional notion, our work suggests that advanced synthesis strategies for preserving the oxygen-rich surface while maximizing surface area will be highly desirable. Furthermore, we believe the design

principles unveiled in this study are applicable for new generation, metal promoted, $ZnZrO_x$ catalysts for further improving catalytic activity and implementation; the future outlook of how we intend to integrate this systematic study with our physical mixing strategy will be discussed as well.

Secondly, I would like to present preliminary data on a mixture catalyst consisting of $Cu/ZnO/Al_2O_3$ and hydrophobic polymers for improving the activity of CO_2 hydrogenation to methanol. Water has been identified as a harmful by-product for CO_2 hydrogenation to methanol as it reduces methanol production and causes deactivation; consequently, selective and expeditious elimination of water from the CO_2-to-methanol reaction system presents a viable pathway towards boosting catalyst performance and stability. It appears that physically mixing $Cu/ZnO/Al_2O_3$ with hydrophobic polymers improves methanol yield. A superior hydrophobic polymer has been identified as well as mass transfer limitations, optimal catalyst-to-polymer weight ratio, and polymer particle size effect. Once the system has been optimized, we hope to patent the technology and commence scale-up for industrial application.

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Electrocatalytic amino acids production from biomass-derivable feedstocks over CNT

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Abstract

The electrocatalytic reductive amination (ERA) uses electrons as reductants and water as the hydrogen source and could be conducted under benign reaction conditions, offering a more sustainable and environmentally friendly strategy for organonitrogen chemicals synthesis. Here, we demonstrate the ERA of biomass-derivable α-keto acids into amino acids using NH_3 as the nitrogen source. Abundant carbon nanotubes (CNTs) were employed as the electrocatalyst, instead of precious or toxic metals that were reported previously. The electrocatalytic activity of CNTs was substantially enhanced by approximately seven times through the facile ball milling (BM) treatment, possibly due to the increased intrinsic defects in the CNTs. We further systematically investigated the effects of applied potentials, concentrations of substrate and ammonia on the BM-CNTs catalyzed ERA in terms of the Faradaic efficiency (FE) and glutamic acid formation rate (FR). A high FE of ~90% with corresponding glutamic acid FR up to 180.9 $\text{mmol}\cdot\text{g}^{-1}_{\text{cat}}\cdot\text{h}^{-1}$ were achieved, and ~60% molar yield of glutamic acid was obtained after 8 h electrolysis after optimization. Detailed electrokinetic analyses indicate that the BM-CNTs catalyzed ERA exhibits a first-order dependence on the substrate and NH_3, with a rate-determining step (RDS) which involves the first electron transfer. Encouragingly, a number of amino acids were prepared by BM-CNTs catalyzed ERA with moderate to high FEs and FRs. Significantly, we efficiently synthesized long carbon chain amino acids, which typically face lower yields using the existing methods.

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Role of Delocalized Electrons on the Doping Effect in Vanadia

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Abstract

Redox chemistry plays an important role in the precise directional production of valuable chemicals. However, mechanistic insight is needed to guide the practical application of accurately controlled redox process. This paper describes how doping improves redox ability of vanadia efficiently for chemical looping oxidative propane dehydrogenation. By clarifying the dynamic redox process of vanadia in virtue of stochastic surface walking method, we found that Mo dopant lowers the phase transformation barrier from defective V_2O_5 towards VO_2. In generated conductive VO_2, Mo dopant governs a series of properties of fifty times oxygen atoms, including oxygen vacancies formation energies, diffusion barriers, surface adsorption strength and corresponding reaction barriers. By contrast, doping in semiconductive V_2O_5 only works on O atoms that direct bind with dopants. Further experiments validated these features make Mo-doped VO_2 dominate in the vanadia catalyzed chemical looping oxidative dehydrogenation of propane with prominently improved performance. Thus, delocalization could be the key to more efficient doped materials and pave the way towards future chemical applications.

Publication List

None

The effect of doping on the properties of NiO_x in perovskite solar cells

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Abstract

Perovskite solar cells (PSCs) as a kind of third-generation photovoltaics have resulted great interest and currently the highest efficiency of single junction perovskite solar cells is over 25%. Hole transporting layer (HTL) that used to charge transfer is an important part of perovskite solar cells. For inverted perovskite solar cells (IPSCs), NiO_X is commonly used as hole transporting material because NiO_X has a wide band gap, stability and good transmittance. However, due to its intrinsic low conductivity and interface reaction, many efforts have been dedicated to optimize NiO_X. Here gadolinium (Gd) doped NiO_X (Gd:NiO_X) nanoparticles were synthesized to study the effect of Gd dopant on the properties of NiO_X and the photovoltaic performance. The Gd doped NiO_X has enhanced conductivity and less defects on its surface. And its film shows great stability which indicates the less reaction between perovskite and NiO_X interface. Therefore, Gd doped NiO_X exhibits improved properties compared with pristine NiO_X. The Gd:NiO_X based devices achieved high power conversion efficiency (PCE) and the best efficiency is 23.6%. Moreover, these devices show good long-term stability and thermal stability. This research demonstrates that Gd:NiO_X is a promising hole transporting material in the future.

Publication List

None

Improving Computational Efficiency of Machine Learning-Based Distributed Predictive Control of Nonlinear Processes Using Feature Selection

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Abstract

While machine-learning-based model predictive control (ML-MPC) for nonlinear processes has been studied in many recent works, the computational cost of ML-MPC for large-scale nonlinear processes with high-dimensional input and output space remains a challenge due to the complexity of both the control problems and the ML models. To reduce the complexity of the control problem, ML-based distributed model predictive control (DMPC) with inter-controller communication has been proposed to improve computation efficiency. However, since full-state information is required for all the controllers in DMPC, a machine learning model that accounts for the states of the entire system is needed, which leads to increased model complexity and computation time in both offline training and online prediction. Therefore, to further improve the computational efficiency of ML-MPC, model reduction techniques such as feature selection will be utilized to develop reduced-order ML models in DMPC. Motivated by the above considerations, we develop reduced-order ML models for large-scale nonlinear processes using feature selection and active learning, and incorporate the ML models within DMPC scheme to improve its computational efficiency.

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Cu-based single atom pair catalysts for CO_2 hydrogenation to methanol

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Abstract

Copper-based catalysts for CO_2 hydrogenation to methanol was promising due to its high CO_2 conversion and industrial application prospect. Cu single-atom catalysts have good methanol selectivity and stability. However, achieving copper single-atom dispersions at metal contents above 2 wt% was challenging. During the reaction, high-loaded copper single atoms tend to agglomerate to form clusters or nanoparticles. Based on the preparation of single-atom Cu/ZrO_2 catalysts by a modified co-precipitation method, we tried to introduce a second metal site to form a single-atom pair with a copper single atom through the isoelectric point adsorption method (CuM/ZrO_2, M=Ni, Ga, Ru, Pt, Pd, Rh) Using its synergistic effect to improve the stability of Cu single atoms during the reaction. Among the catalysts, $CuRh/ZrO_2$ showed the best low-temperature activity and selectivity. Synergistic effect between Cu and Rh single atom pairs effectively inhibits Cu agglomeration and improves the stability of Cu single atoms.

Publication List

none

Modeling of CO_2RR Using Gas Diffusion Electrode by COMSOL Multiphysics

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Abstract

Electrochemical CO_2 reduction reaction (CO_2RR) has drawn plenty of attention as it is able to neutralize carbon emissions and provide a long-term pathway to create energy-dense chemicals from atmospheric CO_2. However, the current density on traditional planar electrodes is limited and thus there is still a long way to go for industrial applications. Recent research proved the ability to enhance current density on the gas diffusion electrode (GDE) by at least an order of magnitude. Here, we have developed a model to simulate the electrochemical CO_2RR by a finite-element-method on COMSOL Multiphysics. After validation, a parametric sweep was performed. The results including partial current densities and species concentration profile were investigated to study the influence of various factors such as pH, electrolyte, applied potential, and electrode porosity. This model can provide some insight into the whole process, especially mass transport, and help with the optimization of the GDE design.

Publication List

none

Non-Faradaic promotion of ethylene hydrogenation under oscillating potentials in fuel-cell reactor

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Abstract

The promotion of catalytic reactions by external stimulation is regarded as a promising tool to enhance heterogenous catalysis beyond catalyst design. The dynamic electric potential is often used to accelerate electrocatalytic process, while its effect on thermocatalysis remain unclear, especially in gas phase. So far, typical promotion tests were conducted in liquid system with electrolyte to conduct current. Here, the dynamic potential promotion of catalytic hydrogenation of ethylene on Pd/C in gas phase were studied in a fuel cell reactor connected with an electrochemical working station, in which the proton exchange membrane serving as solid electrolyte. The effects of static potential and dynamic potential with different frequency and duty cycle were investigated under different gas pressure. The static tests showed a volcano shape curve with peak varying with gas partial pressure. For dynamic tests, with lower ethylene or hydrogen pressure, the optimal promotion happens at a higher frequency and higher duty cycle, with higher enhancement factor. The highest enhancement factor achieved was 6. The reaction order tests show increasing H2 order and decreasing C2H4 order as the static potential becomes more positive. Based on Faradaic efficiency calculation and control experiment, the promotion effect is non-Faradaic.

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Publication List

none

Synthesis of chiral α-amino acids by preserving the chirality of the lignocellulosic biomass-derived substrates

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Abstract

Chiral amino acids are important building blocks of bioactive molecules in chemical, pharmaceutical and agrochemical manufacturing. Most current chemical synthesis routes of α-amino acids, however, result in racemic mixtures of amino acids due to the lack of stereoselectivity. In addition, there have been few works on the synthesis of amino acids from naturally occurring compounds as renewable precursors. The purpose of this work was to develop a chemical pathway to chiral α-amino acids by utilizing the chirality of starting materials, namely hydroxy acids, found in the chiral pool. The two-step strategy involved the use of tosylate reagents to increase the substitutability of the hydroxyl groups, following by the introduction of ammonium acetate to generate the amine groups while the chirality of the carbon atoms was maintained. Initially results demonstrated that the chiral center of the α-carbon was preserved when ethyl L-lactate was used as a model compound. Moreover, the first and second steps could happen with up to 78% and 73% yields, respectively, when 2-butanol was used as a model compound. Methods to directly obtain chiral amino acids from the one-pot reaction between the corresponding hydroxy acids and ammonium acetate with a catalytic amount of tosylic acid are being developed. This work could be a sustainable route to the high-value chiral amino acids from renewable plant-based ingredients.

Publication List

none

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