

The First Joint Thailand-Taiwan Workshop on Catalysis for Carbon Neutrality

Program Book

July 3, 2023

Dr. Poe Lecture Hall

Institute of Atomic and Molecular Sciences, Academia Sinica

Introduction

With the recent global climate issues, controlling CO₂ concentration in the atmosphere is a major target for study in many fields. To build on the global partnership funding of Thailand under Program Management Unit for Human Resources & Institutional Development, Research, and Innovation under N39(S3P19) program 2023 “Development of manpower in international communities for Catalysis/Electrocatalysis for Zero CO₂ Emission (CZCE): Searching a new pathway for the Net-Zero-CO₂ Emissions in Chemical Industry”, we bring together researchers in Taiwan (Institute of Atomic and Molecular Sciences) and Thailand (Vidyasirimedhi Institute of Science and Technology, National Nanotechnology Center National Science and Technology Development Agency) for research exchange and discussion.

We will host The First Joint Thailand-Taiwan Workshop on Catalysis for Carbon Neutrality at Poe Lecture Hall, IAMS on July 3, 2023. In addition to cutting-edge talks by researchers in this challenging field, we will have student poster presentations. We invite those that are interested in participating in our event.

Speakers

Dr. Kuei-Hsien Chen	Academia Sinica, TAIWAN
Assoc. Prof. Chularat Wattanakit	VISTEC, THAILAND
Asst. Prof. Thana Maihom	Kasetsart University, THAILAND
Prof. Chia-Wen (Kevin) Wu	National Taiwan University, TAIWAN
Asst. Prof. Thidarat Imyen	Kyoto University, Japan
Dr. Tsyr-Yan Yu	Academia Sinica, TAIWAN
Dr. Kaito Takahashi	Academia Sinica, TAIWAN

Program

08:30-09:00	Registration
09:00-09:10	Opening: Dr. Jer-Lai Kuo (AS, Taiwan) Session Chair: Dr. Supawadee Namuangruk (NANOTEC, Thailand)
09:10-09:40	Dr. Kuei-Hsien Chen (AS, Taiwan) <i>Photo- and Electro-catalysts for CO₂ Reduction</i>
09:40-10:10	Assoc. Prof. Chularat Wattanakit (VISTEC, Thailand) <i>Alternative route for bioethanol upgrading to fine-chemicals and materials</i>
10:10-10:30	Group Photo and Break
10:30-11:00	Dr. Tsyrr-Yan Yu (AS, Taiwan) <i>The Reorientational Dynamics of A-site Cations in 2D Organic-Inorganic Hybrid Perovskite using Solid-state NMR</i>
11:00-11:30	Asst. Prof. Thana Maihom (Kasetsart University, Thailand) <i>Exploring Adsorption and Reaction Mechanisms on Advanced Materials through Quantum Chemical Computations</i>
11:30-12:30	Poster Presenters (Flash Talk)
12:30-14:30	Lunch and Poster Session Session Chair: Dr. Kaito Takahashi (AS, Taiwan)
14:30-14:50	Asst. Prof. Thidarat Imyen (Kyoto University, Japan) <i>Exploration of CP/MOF glasses as heterogeneous catalysts: The crystal-glass phase transformation for macroscopic shaping of monolithic catalyst</i>
14:50-15:10	Mr. Peeranat Chaipornchalerm (VISTEC, Thailand) <i>Catalytic dehydroisomerization of butane to isobutene over zeolite composites</i>
15:10-15:30	Mr. Kajjana Boonpalit (NANOTEC/VISTEC, Thailand) <i>Graph Neural Networks Accelerated High-throughput Screening of Dual-atom Catalyst for Hydrogen Evolution Reaction</i>
15:30-15:50	Mr. Poobodin Mano (NANOTEC, Thailand) <i>Low C–C Coupling Barriers for Ethanol Synthesis on Boron-Doped Graphyne: Breaking of BEP Relationship and Bond Order Conservation</i>
15:50-16:10	Break

Session Chair: Prof. Chun-Wei Chen (NTU, Taiwan)

16:10-16:30 **Dr. Kaito Takahashi (AS, Taiwan)**

Can electronic structure provide understanding on Carbon-Carbon coupling reaction on B-doped Graphyne?

16:30-17:00 **Prof. Chia-Wen (Kevin) Wu (NTU, Taiwan)**

Metal-Organic Frameworks (MOFs)-Driven Carbon Neutral Society: Heterogeneous Catalysis of Waste Biomass and Plastics Conversion

17:00 **Closing: Dr. Kaito Takahashi (AS, Taiwan)**

Photo- and Electro-catalysts for CO₂ Reduction

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H. T. Lien², Y. F. Huang¹, H. Y. Du², H.-L. Wu², and L.C. Chen²

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ABSTRACT

Photocatalytic CO₂ conversion to hydrocarbon fuels, which makes possible simultaneous solar energy harvesting and CO₂ reduction reaction (CO₂RR), is considered a killing-two-birds-with-one-stone approach to solving the energy and environmental problems. However, the development of solar fuels, or the so-called artificial photosynthesis, has been hampered by the low photon-to-fuel conversion efficiency of the photocatalysts and lack of the product selectivity. Recent advances in development of integrated nanostructured materials have offered unprecedented opportunity for photocatalytic CO₂RR, as depicted in my recent invited review article [1]. Here, selective cases in nanomaterials, especially, atomistic design and synthesis of highly functioning nano-photocatalysts, will be illustrated [2-4]. On the other hand, electrochemical process for CO₂RR using electricity can achieve high Faradaic efficiency. Issues such as throughput, overpotential, stability, and product selectivity remain to be solved. A membrane-based flow cell system with designed electrocatalysts are giving momentum in this direction. Meanwhile, advancements in the in-situ and operando synchrotron radiation-based spectroscopies, including X-ray absorption [5] and X-ray photoelectron spectroscopy (XPS), etc., along with spectroscopy techniques, such as Raman and Fourier transform infrared spectroscopy (FTIR), and scanning electrochemical microscopy [6], have enabled scientists to probe the geometric, bonding and electronic information of the catalyst and obtain atomistic insights into the catalytic surfaces and reaction mechanisms. Selective cases utilizing these probing techniques will be illustrated.

References

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4. M. K. Hussien, and K. H. Chen *et al.*, *Chem. Engineering J.* 430, 132853 (2022).
5. H. T. Lien, and K. H. Chen *et al.*, *Nature Comm.* 11, article number 4233 (2020).
6. H. Y. Du, and K. H. Chen *et al.*, *Nature Comm.* 12, article number 1321 (2021).

Alternative route for bioethanol upgrading to fine-chemicals and materials

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ABSTRACT

Bioethanol obtained from a renewable agricultural resource has become a promising feedstock for producing several chemical compounds and materials, such as ethylene, diethyl ether, and acetic acid. Herein, we illustrate the alternative approach for the catalyst fabrication using zeolites and zeolite composites with hierarchical structures. A series of various hierarchical zeolite frameworks including ZSM-5, MOR, and FER has been successfully synthesized by several approaches such as a simple hydrothermal process and a post-treatment procedure. Interestingly, the designer catalysts exhibit outstanding physicochemical properties in particular high surface area and porosity, suitable acidity, and thermal stability, eventually improving catalytic performances in bioethanol conversion to various chemicals and materials. For example, we also integrated *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies and density functional theory (DFT) calculations to understand the effect of different zeolite frameworks on the catalytic transformation of bioethanol to gain insights into the mechanistic perspectives of bioethanol conversion to ethylene. Apart from ethylene as a desired product from bioethanol, we also illustrate the fabrication of carbon nanotubes (CNTs) from bioethanol via ethylene as an intermediate with high quality and quantity with respect to the traditional direct process of CNTs production from ethanol.

To further develop the industrial catalysts, the rational design of binder-free hierarchical ZSM-5 monolith derived from zeolite@layered double hydroxides (LDH) composites via traditional extrusion and 3D printing technologies has been demonstrated. The designer catalyst applied in bioethanol dehydration boosts ethylene yield by over 96% due to the synergistic effect of zeolites and LDHs. This is the first example illustrating the design of highly efficient catalysts, which can be applied directly in industrial applications. Last but not least, we also illustrate the application of the designer catalysts in the bioethanol dehydration to ethylene on a pilot-plant scale. This example opens up new perspectives on the industrial catalyst design for bioethanol upgrading applications.

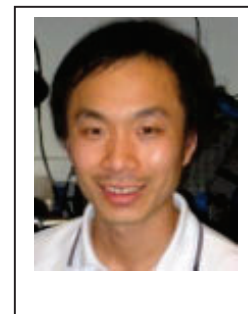
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The Reorientational Dynamics of A-site Cations in 2D Organic-Inorganic Hybrid Perovskite using Solid-state NMR

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ABSTRACT

2D Organic–inorganic hybrid perovskites (OIHPs) have attracted a significant amount of attention for photovoltaic applications owing to their high power-conversion efficiency and improved stability compared to OIHPs. The reorientational dynamics of A-site cations in 2D OIHPs plays an important role in determining their optoelectronic properties. However, limited methods are available for investigating the reorientational dynamics of A-site cations. In this presentation, we will show our ssNMR characterization of the dynamics of A-site cations using isotope strategy. While ^2H NMR analysis reveals the existence of multiple modes of reorientational dynamics of methylammonium (MA), REDOR NMR of 2D OIHPs incorporating (^{13}C , ^{15}N)- MA reflects the averaged dipolar coupling between the two nuclei undergoing different modes of motions. In this work, we clearly reveal the interplay between the rigidity of the organic spacers and the A-site cations dynamics of 2D OIHPs, providing important insights into the materials design.

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Exploring Adsorption and Reaction Mechanisms on Advanced Materials through Quantum Chemical Computations

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ABSTRACT

Quantum chemical computations are invaluable tools for comprehending the intricate mechanistic details of adsorption and reaction processes. Moreover, they provide strategies for the rational design of advanced materials used in adsorption and catalysis. This talk will highlight the application of computational and theoretical approaches to study the adsorption and reaction mechanisms of molecules on advanced materials, such as zeolites, metal-organic frameworks, and carbon materials. The focus will be on elucidating the adsorption processes, unraveling mechanistic and energetic details, and determining reactivity descriptors to predict the binding energies and activation barriers. These results enable the screening and design of promising candidate materials for catalytic applications.

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Exploration of CP/MOF glasses as heterogeneous catalysts: The crystal-glass phase transformation for macroscopic shaping of monolithic catalyst

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ABSTRACT

Coordination polymer (CP) and metal-organic framework (MOF) glasses with preserved short-ranged order have emerged as a new class of materials showing the distinct properties from their crystalline counterparts, for example, optical transparency, mechanical stability, and ionic/electronic conductivities.¹ CP/MOF glasses are obtained by melt-quenching or mechanical milling of crystalline CP/MOFs. Upon heating meltable CP/MOFs above their melting temperature (T_m), the liquid state provides flowability, which allows the macroscopic shaping of catalyst in different sizes and forms without using monolithic supports and binders. For example, 1D CP consisting of zinc ions, orthophosphate, and benzimidazole, namely ZnPBIm was chosen as an example to realize macroscopic shaping of heterogeneous catalyst via its crystal-glass phase transformation. Given the macroscopic form and shapable feature, facile catalyst recovery can be achieved in the liquid-phase levulinic acid esterification with over 90% of catalyst mass recovered.² Moreover, the liquid and glass could be hybridized with catalytically active components. The perspective of hosting metal nanoparticles via the crystal-glass phase transformation will also be discussed.

References

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Catalytic dehydroisomerization of butane to isobutene over zeolite composites

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ABSTRACT

The predominant industrial process for isobutene production as a fuel additive is steam cracking or catalytic cracking; however, it often suffers from a low yield of isobutene with a huge amount of emitted greenhouse gases. To overcome these issues, a novel strategy based on the dehydrogenation of n-butane, which is an endothermic reaction, and butene isomerization with an exothermic feature has been extensively explored. Nevertheless, they are facing with the high operating cost, the fast catalyst deactivation, and the large amount of by-products. Herein, we report the alternative way to rationally design zeolite composites containing as the core-shell structures of different zeolite frameworks for isobutene production in a single process via n-butane dehydroisomerization. For example, the FER/MFI zeolite composite was successfully fabricated by preliminary recrystallization of MFI nanocrystals at the external FER surface, followed by the further growth of the hierarchical structure of MFI, eventually producing the core-shell structure of FER as a core and MFI as a shell. To achieve the high dispersion of hydrogenation sites on a zeolite support, the PtZn incorporated on FER/MFI composite was prepared and they exhibited high catalytic performance in n-butane dehydroisomerization compared to the one containing the PtZn loaded on the bare FER or MFI (17.3% and 2.6% isobutene yield over the PtZn-FER/MFI and the PtZn-FER, respectively). The reason for the improved catalytic activity of the composite relates to the fact that the shell hierarchical MFI could be used to disperse PtZn species, eventually forming small PtZn nanoparticles, which are advantageous for alkane dehydrogenation to alkene [1]. Besides, the excessive acidity of the core FER in composite was suppressed [2] and this would facilitate the conversion of produced butene to isobutene simultaneously. In contrast, the insufficient metal dispersion on the bulk FER surfaces of the isolated FER (PtZn-FER) led to the formation of agglomerated PtZn particles which were ineffective in butane dehydrogenation. Moreover, the excessive acidity of PtZn-FER enabled the catalytic cracking of butene, resulting in low isobutene yield. This example opens up the perspective of the rational design of zeolite composites with fine-tuning acid and shape-selective properties for isobutene production.

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Graph Neural Networks Accelerated High-throughput Screening of Dual-atom Catalyst for Hydrogen Evolution Reaction

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ABSTRACT

The flexible tuning ability of dual-atom catalysts (DACs) makes them an ideal system for a wide range of electrochemical applications. However, the large design space of DACs and the complexity in the binding motif of electrochemical intermediates hinder the efficient determination of DAC combinations for desirable catalytic properties. A crystal graph convolutional neural network (CGCNN) was adopted for DACs to accelerate the high-throughput screening of hydrogen evolution reaction (HER) catalysts. From a pool of 435 dual-atom combinations in N-doped graphene (N₆Gr), we screened out two high-performance HER catalysts (AuCo@N₆Gr and NiNi@N₆Gr) with excellent HER, electronic conductivity, and stability using the combination of CGCNN and density functional theory (DFT). Furthermore, comprehensive DFT studies were conducted on these two catalysts to confirm their outstanding reaction kinetics and to understand the cooperative effect between the metal pair for HER. To obtain ideal hydrogen binding in AuCo, the inert Au weakens the strong hydrogen binding of Co, while for the NiNi, two weakly binding Ni cooperate. The present protocol was able to select the two catalysts with different physical origins for HER and can be applied to other DAC catalysts, which should hasten catalyst discovery.

References

1. K. Boonpalit, Y. Wongnongwa, C. Prommin, S. Nutanong, S. Namuangruk, **Data-Driven Discovery of Graphene-Based Dual-Atom Catalysts for Hydrogen Evolution Reaction with Graph Neural Network and DFT Calculations.**, *ACS Applied Materials & Interfaces*, 15 (10), 12936-12945. (2023)

Low C–C Coupling Barriers for Ethanol Synthesis on Boron-Doped Graphyne: Breaking of BEP Relationship and Bond Order Conservation



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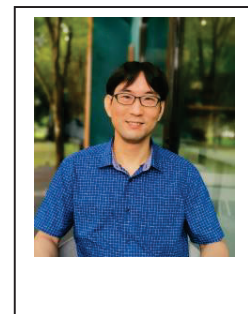
ABSTRACT

The development of CO₂ utilization technologies is inevitable to realize the carbon neutral society. The electroreduction is one of the promising strategies in turning waste CO₂ into valuable products, though it is still hard to gain the multi-carbon products in practical. In this study, we theoretically demonstrated that the B doped graphyne (B-GRY) can become a suitable platform for CO₂ activation as well as CO₂ reduction reaction producing C₂H₂OH product with low limiting potential of 0.53 V. The activeness of the B-GRY is ascribed to the formation of the π orbital localized around the acetylene near the Fermi level, which facilitates the efficient electron transfer. Remarkably, the B doping not only enhances the binding of key intermediate CO but also significantly lowers the activation barrier of C-C bond formation, which breaks the general understanding of the Bell–Evans–Polanyi (BEP) relation where the stronger binding was expected to increase the activation energy. Moreover, for the first time, we utilized the concept of integrated crystal orbital bond index (ICOBI) to analyze the C-C bond formation mechanism and confirmed that the bond order is conserved along the C-C coupling process. We believe that this finding will provide a new direction which differs from the previous understanding that mainly focused on the weakening of CO to promote C-C coupling.

References

1. P. Mano, S. Namuangruk, & K. Takahashi, *The Journal of Physical Chemistry C*, 127, 16, 7683–7694 (2023).

Can electronic structure provide understanding on Carbon-Carbon coupling reaction on B-doped Graphyne?



Poobodin Mano¹, Supawadee Namuangruk¹, and Kaito Takahashi²

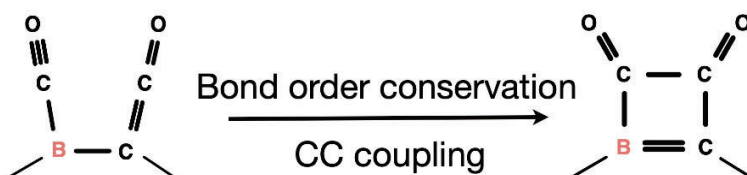
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ABSTRACT

Due to the issue of global warming, efficient utilization of CO₂ has been an important topic. Electrocatalytic reduction of CO₂ to C₂₊ products such as C₂H₄, C₂H₅OH, or C₃H₇OH is an ideal solution. However, applications have been hindered by the slow kinetics due to the very high barrier of the Carbon-Carbon coupling (CC coupling) reaction. Here, we take a look at the important electronic states of the adsorbates in the CC coupling reaction using theoretical calculations.

In many previous studies, we find that for efficient lowering of the CC coupling reaction barrier, an asymmetry is required: *CO+*COH→*OC-COH, or *CO+*CHO→*OC-CHO. For the *CO+*CO→*OC-CO coupling reaction, studies have shown that difference oxidation state of copper surface can reduce the C-C coupling barrier to 0.7 eV. Here we looked at the reaction on boron doped graphyne, which is a new allotrope of carbon containing both sp² (benzene knots) and sp (acetylene linkers) hybridization, we found the CC coupling barrier to be very low at 0.4 eV. Analyzing the bond order index along the reaction path, we found that the acetylene linkers change from sp to sp² to sp³ hybridization as the reaction proceeds. This flexible change of the acetylene linker allows for the efficient formation of the *OCCO intermediate. We believe such a new mechanism for neutral CC coupling will open up new ideas for the efficient production of C₂₊ products.



References

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Metal-Organic Frameworks (MOFs)-Driven Carbon Neutral Society: Heterogeneous Catalysis of Waste Biomass and Plastics Conversion

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ABSTRACT

Scientific innovation in various fields is surely necessary to achieve carbon neutrality by 2050. To reduce carbon dioxide (CO₂), seven approaches including de-fossil resources, switch to renewable energy, etc. have been proposed. Meanwhile, nanoporous metal-organic frameworks (MOFs) have been well known and have shown great potential in catalysis and energy applications owing to their high surface areas, controllable composition, and tunable surface functionalities. In this talk, I will focus on MOFs-driven carbon neutral society by introducing MOFs in waste biomass and plastics conversion. (1) For heterogeneous catalysis, we synthesize a heterogeneous Bi-BTC catalyst for the conversion of bio-based 2,5-dimethylfuran and acrylic acid to para-xylene with a promising yield (92%), under relatively mild conditions (160 °C, 10 bar) with low reaction energy barrier (47.3 kJ/mol). The proposed reaction strategy also demonstrated remarkable versatility for furan derivatives such as furan and 2-methylfuran. (2) For plastics conversion, polyethylene terephthalate (PET) has been extensively used for fabrication of various packaging materials, creating million tons of waste per year. Degrading and recycling PET waste has been identified as a prominent issue. Herein, we demonstrate an effective process to chemically convert PET to bis(2-hydroxyethylterephthalate) (BHET) through the use of metal azolate framework-6 (MAF-6) as a catalyst in the presence of ethylene glycol. A high 92.4% conversion of PET and 81.7% yield of BHET at 180 °C for 4 h was achieved. We have also hypothesized a mechanism for the high conversion and yield of PET glycolysis reaction catalyzed by MAF-6.

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List of Poster Presentations

Board number	Presenter	Title of the poster
01	Chih-Yang Huang	Charge Density Manipulation by Transition Metal Heteroatoms on Tungsten Trioxide for Photocatalytic CO ₂ Reduction
02	Klichchupong Dabsamut	Exploration of B-doped Graphyne Family as Efficient Metal-Free Catalyst for C-C Coupling
03	Tsung-Han Tsai	Simulating C-C Coupling Reaction on Gas Diffusion Electrode Surface Modified with Sodium Perfluoro-1-pentanesulfonate Using DFT/MM
04	Watinee Nunthkitguson	Simultaneous H ₂ production and biorefinery using nickel-decorated carbon nanotubes (CNTs) derived from bioethanol as electrocatalysts
05	Tsai Yu Lin	Doped Molybdenum Disulfide Thin Films for CO ₂ Photoreduction
06	Kajjana Boonpalit	Graph Neural Networks Accelerated High-throughput Screening of Dual-atom Catalyst for Hydrogen Evolution Reaction
07	Wei-Lun Liang	The Possibility of Linker Rotation Impact to CO ₂ RR in MOF-253 Materials: The Comprehensive Discovery by Force Field and DFT Simulation
08	Narasiri Mainewklang	Accelerated synthesis of hierarchical FER nanoneedles with the ETL seed-assisted approach
09	Philip Anggo Krisbiantoro	Chemical recycling of PET via glycolysis over solvent-free mechanochemically synthesized spinel ferrites
10	Sorasak Klinyod	Tailoring Implanted Ti Active Species in Various Zeolite Frameworks for Methyl Oleate Epoxidation
11	Babasaheb Matsagar	An economically feasible sustainable method for the synthesis of biomass-derived tri(furylmethane) derivatives for electrochromic applications
12	Anittha Prasertsab	Efficient hydrogenation of 5-hydroxymethylfurfural (5-HMF) to bis(hydroxymethyl)tetrahydrofuran (BHMTHF) under mild conditions over metals supported on hierarchical zeolites

13	Lalida Waura-angkura	Depolymerization Kinetic of Dealkaline Lignin via Microreactor-assisted Electrochemical Advanced Oxidation Process
14	Ploychanok Iadrat	Nanocrystalline BEA-CNT composites with highly metal dispersion obtained via inter-zeolite transformation for antibacterial application
15	Muhammad Yusuf Fakhri	Improved thermoelectric performance of p-type tin monosulfide polycrystalline through metal precipitates

Charge Density Manipulation by Transition Metal Heteroatoms on Tungsten Trioxide for Photocatalytic CO₂ Reduction

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ABSTRACT

In the past decades, the greenhouse gases and renewable energy topics have attracted attention because of the expeditious climate change. Photocatalytic (PC) CO₂ reduction into value-added molecules can be a potential method to address the abovementioned problems. However, PC CO₂ reduction suffers from the low production rate, which contributed to low surface electron density. That is electron-rich surface is essential for superior catalytic activity. Engineering the surface defects such as point defects is an effective way to manipulate the local electronic structure and activate the inert surface. Point defect can be introduced by doping heteroatoms and the generation of vacancies. In the field of catalysis, heteroatom doping or single-atom catalysts (SACs) is a rapidly developing approach due to its unique electronic properties to boost catalytic performances. Although most studies on the SACs have used highly active noble metals, their high cost limits their utilization for industry applications. So, we choose transition metals with the 3d electronic configuration (i.e., Cr, Fe, and Ni atoms) as the candidate heteroatoms. However, the influences of transition metal heteroatom doping on charge density distribution haven't been clearly studied yet. Herein, we theoretically predict and experimentally confirm the heteroatom-assisted charge density re-distribution on the surface of tungsten trioxide (WO₃). Density functional theory (DFT) calculations show that the anchored transition metals play a role as electron contributors to the neighbor atoms. Synchrotron-based x-ray absorption near-edge structure (XANES) and Fourier transform extended x-ray absorption fine structure (FT-EXAFS) are performed to prove the presence of single atoms thereon the WO₃ surface. Further, the x-ray photoelectron spectroscopy (XPS) technique is used to find the direction and amount of transferred charge. Finally, the PC CO₂ reduction yields also unveil that the production rate is proportional to the amount of transferred (donated) electron. This study provides insights into the correlation between CO₂ conversion and the surface charge distribution, implying the significance of the surface charge density in the field of catalysis.

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P02

Exploration of B-doped Graphyne Family as Efficient Metal-Free Catalyst for C-C Coupling

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ABSTRACT

The electrocatalytic CO₂ reduction reaction (CO₂RR) holds great promise to produce valuable C₂₊ chemicals at mild conditions. However, the search for catalysts that are both eco-friendly and cost-effective is essential for the improvement of this field.

Metal-free catalysts provide a financially and environmentally friendly solution for CO₂RR, eliminating the need for expensive metals while reducing environmental impact. Graphyne is a metal-free carbon-based material featuring *sp-sp*² hybridized carbon bonds. These unique bonds provide enhanced reactivity and electron transfer capabilities, making them an attractive option for CO₂RR.

Earlier this year, Mano *et al.*¹ proposed using B-doped γ -graphyne, which exhibited a low carbon-carbon (C-C) coupling barrier of 0.46 eV, as a potential catalyst for ethanol production. Building upon this study, we extend that idea by conducting theoretical investigations on a variety of B-doped graphyne families. Employing density functional theory (DFT), our findings indicate that out of the 15 different structures studied, four exhibit promising potential as CO₂RR catalysts, including 4,12,2-, sR-, γ -, and 6,6,12-graphynes. Among them, B-doped 4,12,2-graphyne demonstrates the highest efficiency as a CO₂RR catalyst for C-C coupling, with a negative value of heat of reaction (2*CO → *OCCO) and the lowest C-C coupling barrier of 0.337 eV. Furthermore, our research reveals a correlation between the heat of reaction (2*CO → *OCCO) for each B-doped graphyne structure and the average area of the pore formed by C_{sp} linkers at the active reaction site. Ultimately, this study presents a promising approach for developing efficient metal-free electrocatalysts for CO₂ reduction.

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P03

Simulating C-C Coupling Reaction on Gas Diffusion Electrode Surface Modified with Sodium Perfluoro-1-pentanesulfonate Using DFT/MM

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ABSTRACT

This study employed molecular dynamics simulations at 300K NVT to investigate the C-C coupling reaction on a Cu(111) electrochemical electrode surface modified with sodium perfluoro-1-pentanesulfonate (NaPFPS). Density functional theory was utilized to simulate the OC-CO and OC-COH coupling reactions, revealing that protonated *COH is more prone to coupling with *CO. By investigating the diffusion of *CO and *COH on the gas/solid electrode interface and the influence of their adsorption encounter orientation, it was observed that both diffusion energies were relatively small. Furthermore, when OH was oriented towards *CO, the coupling energy and reaction energy were further reduced. Overall, this study provided valuable insights into the C-C coupling reaction on a NaPFPS-modified electrochemical electrode, including crucial information about the modification conditions and reaction mechanism. These findings provide the microscopic foundation for the design and optimization of gas diffusion electrodes modified with sulfonated perfluoro-polymer, offering significant insights for its future applications.

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Simultaneous H₂ production and biorefinery using nickel-decorated carbon nanotubes (CNTs) derived from bioethanol as electrocatalysts**W. Nunthakitguson. A. Sohail, S. Tiwtusthda, P. Chaipornchalen, A. Thivasasith, and C. Wattanakit***

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ABSTRACT

The development of novel biorefinery and hydrogen production technologies is one of the most interesting topics in modern science and technology. To date, there are several proposed strategies that have been used in both biorefinery and hydrogen production, in particular, using electrochemical processes. To achieve the high electrocatalytic performances of these processes with minimizing energy consumption, various types of electrocatalysts applied in both anodic and cathodic compartments have been extensively designed. Among several types of catalysts, the Ni-based materials are considered as the most important catalysts for biorefinery such as the electrochemical oxidation of 5-hydroxymethylfurfural (5-HMF); however, they are lacking in term of catalyst stability, eventually leading to a short catalyst lifetime.^[1,2] To overcome this issue, various carbon based-materials have been coupled with Ni nanoparticles to enhance its catalytic performance because of the high conductivity and the appropriate electronic structure of active sites. In this contribution, we report the fabrication of nickel nanoparticles supported on carbon nanotubes (NiCNTs) as electrocatalysts. In this case, the CNTs can be produced via chemical vapor deposition (CVD) employing bioethylene as a carbon source derived from bioethanol dehydration. In both anodic and cathodic compartments, the fabricated NiCNTs electrodes were applied as electrocatalysts for efficient HMF oxidation and hydrogen generation, respectively. As can be seen in Figure 1, the kinetic curves of HMF electrooxidation over NiCNTs at a constant potential of 1.45 V versus NiCNTs/NF were obtained. It was found that HMF oxidation occurs mechanistically via the HMFCA as an intermediate, which can be then transferred to FFCA. Interestingly, after two hours of reaction, FDCA selectivity increased dramatically to 95%, with 100% of HMF conversion. Simultaneously, the cathodic portion initially produced hydrogen at a modest rate of 21 $\mu\text{mol. min}^{-1}$, which increased substantially to 150 $\mu\text{mol. min}^{-1}$ when the reaction time was extended to 2 hours as depicted in Figure 1B. This study presents a rational design of a highly efficient electrocatalyst utilized in an electrochemical process to convert simultaneously biomass-derived compounds to chemicals together with clean hydrogen production.

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Doped Molybdenum Disulfide Thin Films for CO₂ Photoreduction

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ABSTRACT

Artificial photosynthesis is a promising technique that can reduce the CO₂ levels via producing energy., simultaneously. Through light irradiation, photocatalyst CO₂ reduction can convert carbon dioxide molecules into valuable solar fuel¹. However, photocatalyst for CO₂ reduction exists great challenges, i.e., selectivity and low efficiency. It seems increasing the active sites of catalyst and studying the reaction pathways would deal with the above-mentioned issues. In this regard, we propose introducing transition metal dopants into the crystal structure of inert MoS₂ to modify its basal plane for CO₂ activation. Beyond active site modulation, dopants can further change the electronic structure resulting in a tunable opto-electrical properties and stabilizing the favored intermediates. Wafer-scale MoS₂ ultrathin films are synthesized by thermal decomposition method. Raman scattering spectroscopy is widely used to investigate the lattice vibrational modes of the pristine and doped MoS₂. Based on the results, this work demonstrated that the thermal decomposition method is a promising way to grow doped wafer-scale transition metal chalcogenides ultrathin films.

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Graph Neural Networks Accelerated High-throughput Screening of Dual-atom Catalyst for Hydrogen Evolution Reaction

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ABSTRACT

The flexible tuning ability of dual-atom catalysts (DACs) makes them an ideal system for a wide range of electrochemical applications. However, the large design space of DACs and the complexity in the binding motif of electrochemical intermediates hinder the efficient determination of DAC combinations for desirable catalytic properties. A crystal graph convolutional neural network (CGCNN) was adopted for DACs to accelerate the high-throughput screening of hydrogen evolution reaction (HER) catalysts. From a pool of 435 dual-atom combinations in N-doped graphene (N₆Gr), we screened out two high-performance HER catalysts (AuCo@N₆Gr and NiNi@N₆Gr) with excellent HER, electronic conductivity, and stability using the combination of CGCNN and density functional theory (DFT). Furthermore, comprehensive DFT studies were conducted on these two catalysts to confirm their outstanding reaction kinetics and to understand the cooperative effect between the metal pair for HER. To obtain ideal hydrogen binding in AuCo, the inert Au weakens the strong hydrogen binding of Co, while for the NiNi, two weakly binding Ni cooperate. The present protocol was able to select the two catalysts with different physical origins for HER and can be applied to other DAC catalysts, which should hasten catalyst discovery.

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P07

**The Possibility of Linker Rotation Impact to
CO₂RR in MOF-253 Materials: The
Comprehensive Discovery by Force Field and DFT
Simulation**



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ABSTRACT

Although metal-organic frameworks (MOFs) are a class of eye-catching materials for decades, how linkers' rotation impacts the applications remains for exploration. Here, the linker, bipyridine dicarboxylate (bpydc), rotation took place in the research of the gas adsorption in the MOF-253 under 1000K as an example. This phenomenon extended the reaction investigation in our previous research¹. The simulated PXRD, the MD, and the DFT calculations examine the possibility of bpydc rotation. Further, a new vision for the CO₂RR catalytic mechanism, the metal dimer reactions could be realized after the linker rotation.

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Accelerated synthesis of hierarchical FER nanoneedles with the ETL seed-assisted approach

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ABSTRACT

The rational design of zeolite nanostructures in a molecular level is an interesting task because it has an essential impact on zeolite properties and catalytic performances in many reactions. However, it still suffers from some drawbacks because most synthesis approaches require complex procedures and time-consuming processes. To overcome these problems, the development of the new synthesis approach with the combination between one-step and fast synthesis approaches would be one of the promising research topics. In this contribution, the rapid synthesis of hierarchical ferrierite nanoneedles has been demonstrated using chlorine chloride as a structure-directing agent and a sodium cation (Na^+) as the mineralizing agent with the ETL seed-assisted approach via hydrothermal process. Interestingly, by adding a small amount of ETL seed, the crystallization growth could be accelerated, and the FER framework can be directly formed due to the aid of the similar building units (CBUs), namely *mor*, which is the main units of both FER and ETL zeolites. In contrast, no crystalline phase could be formed without adding ETL seed at the early stage of synthesis. The literally different morphologies between without and with adding ETL seed were observed. The bulk and irregular shape was obtained in case of without adding ETL seed, while the nanoneedles shape was obtained when adding ETL seed. In addition, the use of other zeolite frameworks as seed-assisted sources for the synthesis of hierarchical FER nanoneedles has been investigated to confirm that *mor* CBUs play a critical role in FER formation. Finally, the ethanol dehydration has been performed to illustrate the beneficial catalytic aspect of the synthesized hierarchical FER nanoneedles.

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Chemical recycling of PET via glycolysis over solvent-free mechanochemically synthesized spinel ferrites



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ABSTRACT

In the present study, the solvent-free mechanochemically synthesized MFe_2O_4 ($M = Co, Ni, Cu, \text{ and } Zn$) spinel was used for polyethylene terephthalate (PET) glycolysis. While all catalysts were active for PET glycolysis to produce bis(2-hydroxyethyl) terephthalate (BHET), the catalytic activity was found to be correlated with the Lewis acid strength of the M^{2+} , i.e., catalysts with higher Lewis acid strength of M^{2+} tended to give higher catalytic activity. Although $CoFe_2O_4$ was the second-best in terms of yield of BHET, it exhibited the highest saturation magnetization and thus can be employed as a magnetic catalyst for PET glycolysis without the need for surface modification. It was observed that the reaction over $CoFe_2O_4$ had an apparent activation energy (E_a) of 188 kJ mol^{-1} and can be used at least five times. A simulation conducted using Aspen Plus[®] software indicated that scaling up the process is feasible.

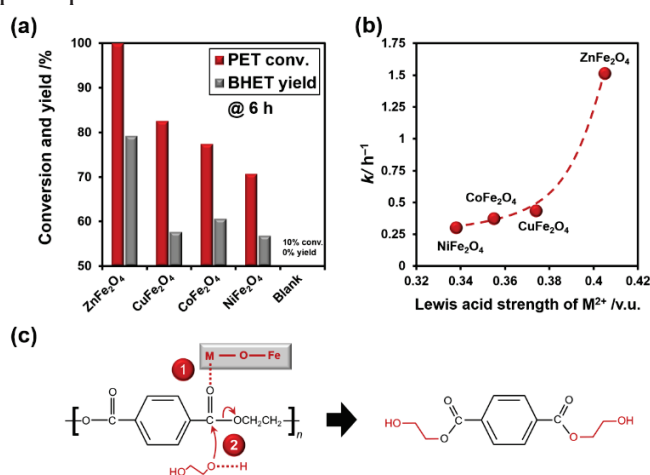


Figure 1. (a) Catalytic performance of MFe_2O_4 for PET glycolysis, (b) First-order rate constant (k) for PET glycolysis over MFe_2O_4 as a function of Lewis acid strength of M^{2+} , and (c) Plausible mechanism for PET glycolysis over MFe_2O_4 . Reaction conditions: catalyst weight, 0.2 g; EG weight, 30 g; PET weight, 5.0 g; reaction temperature, $190 \text{ }^\circ\text{C}$; and reaction time, 6 h.

Keywords: PET; Glycolysis; Metal ferrite; Spinel; Mechanochemical; Aspen Plus[®]

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Tailoring Implanted Ti Active Species in Various Zeolite Frameworks for Methyl Oleate Epoxidation

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ABSTRACT

It is well-known that incorporating transition metals, especially Ti atoms, into the zeolite's frameworks is the most promising method for creating a redox zeolite to catalyze either acid-catalyzed or redox reactions.^[1,2] In this contribution, we demonstrate the isomorphic substitution of the Ti atom in the three different zeolite topologies including Ti-FER, Ti-ZSM5, and Ti-BEA, using the post-synthetic method. The two consecutive reactions of the dealumination and subsequent titanation are employed for incorporating efficiently the Ti atom into the zeolite frameworks. Such three different Ti-containing zeolite topologies are chosen to examine the influence of the zeolite frameworks on the efficiency of the implanted Ti active redox sites. It is observed that the zeolite topology can directly affect the structure of the embedded Ti active sites, confirmed by XAS and UV-Vis DRS techniques, eventually changing the electronic property of the incorporated Ti species. It is found that the Ti-BEA topology is entirely composed of isolated tetrahedrally coordinated Ti active sites. In contrast, the variance of the Ti species, such as the isolated four-coordinated Ti sites, polymeric Ti species,^[3] and Ti anatase, verified by XAS and UV-Vis DRS technique, can be observed in both Ti-FER and Ti-ZSM5 catalysts. To gain insights into the catalytic efficiency related to the electronic property of implanted Ti species, the as-synthesized catalysts are applied to catalyze the methyl oleate (MO) epoxidation to evaluate the catalytic performance of Ti active species. The superior catalytic performance (~70% MO conversion and ~80% epoxide (EP) selectivity) of the Ti-BEA catalyst can be found when comparing with the Ti-ZSM5 (~30% MO conversion and ~45% EP selectivity) and the Ti-FER (~0.5% MO conversion and ~5% EP selectivity). These observations should be associated with the differentiation of an electronic property of Ti species induced by the zeolite topologies toward changing the efficiency of Ti active species. Moreover, the differentiation of the electronic property of the Ti active species can influence the product distribution of MO epoxidation. The results indicate that the Ti-ZSM5 zeolite facilitates the further transformation of the epoxide compound into the hydrolyzed methyl 9,10-dihydroxy stearate (MDI) product. In contrast, the undesired product of MDI can be suppressed when the isolated Ti active site in BEA zeolite is applied as a catalyst. This study can disclose the effect of zeolite topology on the electronic property of implanted Ti active species, leading to rational design of the Ti-containing in the suitable zeolite framework.

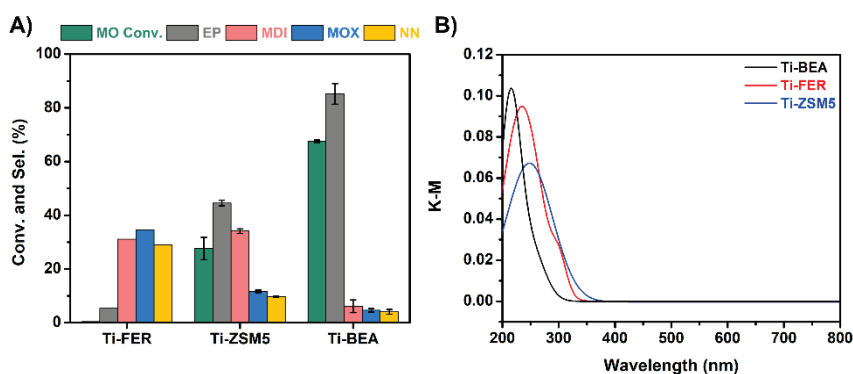


Figure 1. A) Catalytic performance in methyl oleate (MO) epoxidation of different catalysts and B) UV-Vis spectra of as-synthesized catalysts.

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Acknowledgment

This work was financially supported by the Vidyasirimedhi Institute of Science and Technology (VISTEC), the National Research Council of Thailand (NRCT), Thailand Science Research and Innovation (TSRI), and the Program Management Unit for Human Resources & Institutional Development, Research and Innovation (grant number: B39G660027).

P11

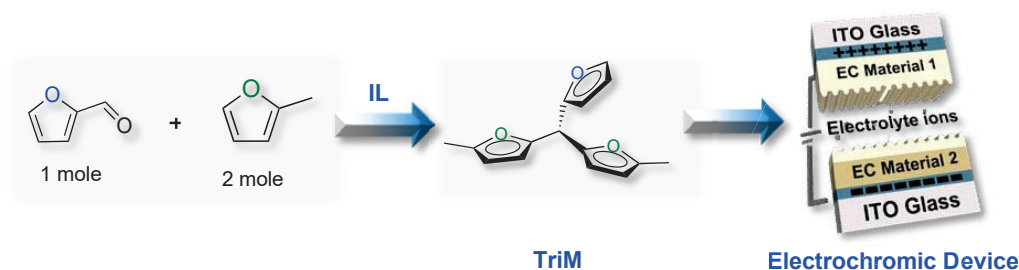
An economically feasible sustainable method for the synthesis of biomass-derived tri(furylmethane) derivatives for electrochromic applications



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Herein we demonstrated an environmentally benign, economically feasible sustainable synthesis method of biomass-derived tri(furyl)methane (TriM) derivatives using 2-hydroxy-N, N-dimethylethane ionic liquid (IL) catalyst. The reactions were carried out at 60 °C with 2-methylfuran and furfural, and with 2-methylfuran and 5-hydroxymethylfurfural (HMF) showed complete conversion of furfural and HMF, respectively. The IL catalyst was easily recyclable due to its insolubility in the final reaction solution. More importantly, the reactions were performed with 10 wt% substrate concentration without using any additional solvent, which is highly beneficial concerning the cost of the process. The IL showed higher product selectivity than previously reported catalysts.¹ Higher substrate concentration use, solvent system selection flexibility, easy IL catalyst synthesis,² and catalyst recyclability are the potential advantages of the developed reaction system. In addition, the TriM was successfully utilized for electrochromic applications and showed high coloration efficiency (1796 cm²/C).



Scheme Application of biomass-derived TriM for fabricating the electrochromic device.

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Efficient hydrogenation of 5-hydroxymethylfurfural (5-HMF) to bis(hydroxymethyl)tetrahydrofuran (BHMTHF) under mild conditions over metals supported on hierarchical zeolites
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ABSTRACT

The selective hydrogenation of biomass-derived 5-hydroxymethylfurfural (5-HMF) is of essential importance to produce a variety of high value products and derivative chemicals such as 2,5-bis(hydroxymethyl)furan (BHMTHF), and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF).¹ However, it is difficult to achieve the high BHMTHF yield since 5-HMF is reactive and then it is converted to a variety of by-products such as 5-methylfurfuryl alcohol (5-MFA), 2,5-dimethylfuran (DMF), and 5-methylfurfural (MF) because it contains three functional groups of furan ring, carbonyl group (C=O), and hydroxyl group (O-H). Moreover, the BHMTHF production often suffers from high operating cost due to using high hydrogen pressure and temperature. Recently, the design of an ideal catalyst based on noble metals under high hydrogen pressure condition², for example, Pt, Ru, and Pd, has been extensively investigated. To overcome these problems, in this work, the selective transformation of 5-HMF to BHMTHF using highly Ru dispersed on hierarchical MFI zeolite surfaces (Ru-Hie-MFI) was studied under mild conditions in the presence of sodium borohydride (NaBH₄) as the low-cost hydrogen source. As illustrated in Figure 1, the catalytic performance of Ru-Hie-MFI in the 5-HMF hydrogenation exhibited a high yield of BHMTHF (> 80%). The observations suggested that the hierarchical zeolite surfaces can promote the high dispersion of Ru nanoparticles, eventually improving the catalytic reaction of 5-HMF hydrogenation to selectively produce BHMTHF and the use of NaBH₄ as a hydrogen storage can facilitate the conversion of aldehyde group of 5-HMF to desired products. This example illustrates the rational design of a heterogeneous catalyst for the highly selective 5-HMF hydrogenation to BHMTHF and opens up a new perspective of converting biomass-based resources to high-value added products in the absence of severe conditions.

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Depolymerization Kinetic of Dealkaline Lignin via Microreactor-assisted Electrochemical Advanced Oxidation Process

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ABSTRACT

In light of aromatic compounds recovery from lignin, the largest source of renewable aromatic compounds, this work focuses on efficient depolymerization of dealkaline lignin using the electrochemical advanced oxidation process (EAOP) under ambient conditions in a continuous-flow microreactor system. As hydroxyl radicals generated from water at the anode are the key to the EAOP, yet dealkaline lignin has extremely low solubility in water, the effects of water-miscible co-solvents, e.g., N, N-dimethylformamide (DMF), acetonitrile (MeCN), and ethanol (EtOH), on the depolymerization kinetics were investigated. It was revealed that the degradation of dealkaline lignin followed a pseudo-first-order kinetic model, where the rate constant in MeCN ($3.3 \times 10^{-3} \text{ s}^{-1}$) > DMF ($1.2 \times 10^{-3} \text{ s}^{-1}$) > EtOH ($0.9 \times 10^{-3} \text{ s}^{-1}$). The same trend was also observed in the lignin model compound representing β -O-4 linkage. Among the co-solvent systems, dealkaline lignin in the water/MeCN system demonstrated the highest conversion of 72% within 100 seconds of residence time with a 1 mA applied current. In addition, from the mechanistic study, it was elucidated that the depolymerization of β -O-4 in water/EtOH primarily followed C_{α} -OH activation, C_{α} -H activation, and C_{α} -OH oxidation pathways.

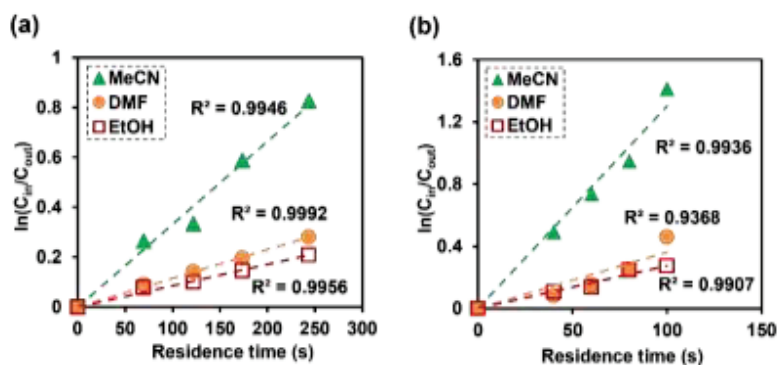
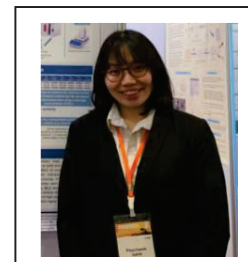


Figure 1 Linear plot of the pseudo-first-order kinetic model for the depolymerization of (a) dealkaline lignin and (b) β -O-4 model compound. Reaction conditions: Co-solvent, 30% vol. in water; initial concentration, 130 and 100 ppm (for dealkaline lignin and β -O-4 model compound, respectively); and applied current of 1 mA.

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Nanocrystalline BEA-CNT composites with highly metal dispersion obtained via inter-zeolite transformation for antibacterial application



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ABSTRACT

The rational design of combined carbon nanotubes (CNTs) and zeolites as composites is a promising strategy to fine-tune hydrophobic and hydrophilic properties of zeolite surfaces, eventually improving antibacterial activity due to the high dispersion in antibacterial mediums and interaction with bacterial cells. In this contribution, the Ag incorporated nanocrystalline BEA-carbon nanotubes (CNTs) was successfully synthesized via the one-pot inter-zeolite transformation¹ of the micron-sized FAU-CNTs composite in the simultaneous presence of Ag precursors using tetraethylammonium hydroxide (TEAOH) as a structure-directing agent (SDA). The zeolite inter-conversion mechanism was systematically explored by varying the crystallization time. It was found that the inter-zeolite transformation process undergoes through an amorphous intermediate with the change of crystal morphology in the solid phase. Interestingly, the redispersion of metal particles was observed after the inter-zeolite transformation process resulting in the high dispersion of metal particles over BEA nanocrystals. Notably, it was revealed that the Ag sites are stabilized by the CNTs interaction leading to the availability of active Ag⁺ ions. Moreover, the CNTs qualities were not significantly changed after the zeolite inter-conversion process. Remarkably, the synthesized Ag incorporated BEA-CNTs composite exhibited the high antibacterial activity against *Escherichia coli* (*E. coli*)² according to the existence of highly active Ag⁺ species and high CNTs quality with an improved interaction between the antibacterial material and *E. coli* cells. This first example opens up the rational design of zeolite-CNTs composites with high metal-dispersion for biomedical applications.

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Improved thermoelectric performance of p-type tin monosulfide polycrystalline through metal precipitates



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ABSTRACT

Thermoelectric generator is the future renewable energy source enabling direct conversion from heat into the electricity for dealing with carbon footprint issue in the atmosphere. Tin monosulfide (SnS) has emerged as a promising thermoelectric material due to its abundance, low toxicity, and potential for high performance. It exhibits anharmonicity that softens chemical bonds, resulting in ultralow thermal conductivity at moderate temperatures¹. However, the challenge lies in the significant decrease in electrical conductivity observed in polycrystalline SnS compared to its single crystal counterpart². In this study, we successfully synthesized polycrystalline p-type SnS through a precipitate design approach under metal-rich conditions. Under the moderate temperature solid state reaction process at 973 K, the SnS polycrystalline was synthesized with small grain sizes, effectively reducing thermal conductivity. Although having the large grain size alone did not significantly enhance the electrical conductivity, the metal precipitates decorating the grain boundaries exhibited a remarkable improvement in electrical conductivity. We demonstrated that with two different metals the high power factor was achieved approximately 2.5 and 4 $\mu\text{W}/\text{cmK}^2$ at 473 K for tin and silver rich conditions respectively. This corresponds to a relatively high thermoelectric figure of merit (zT) of nearly 0.2 at 473 K for tin and 0.35 at 523 K for silver, which are relatively high for low-temperature applications involving this class of materials. Therefore, the precipitate strategy presented in this work is promising for enabling high-performance polycrystalline tin monosulfide.

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