제 140 차
대한화학회 물리화학분과 여름 심포지엄

일시: 2023 년 6 월 19 일(월) – 21 일(수)
장소: 부산 해운대 한화리조트

주 최: 대한화학회 물리화학분과회

공동주최:

IBS 첨단 반응동역학 연구단
고려대학교 분자 분광학 및 동력학 연구단 (IBS, CMSD)
KENTECH 광에너지 전환 연구실 (리더연구)
경상국립대학교 광화학 나노소재 전문 핵심연구지원센터
광화학 나노소재 에너지 환경 기초연구실(BRL)
부산대학교 기초연구실 (BRL)
중앙대학교 생물리광화학 창의인재 양성사업팀 (BK21)
중앙대학교 세포화학동력학 창의연구단 (리더연구)
POSTECH 양자동역학연구센터 (SRC)
연세대학교 지속가능 화학 교육연구단 (BK21)
강원대학교 강원방사선융복합연구지원센터 (KRCRSC)
경북대학교 혁신화학소재 교육연구단 (BK21)
POSTECH 분자과학교육연구단 (BK21)
부산대학교 에너지융합기술교육연구단 (BK21)

후 원:

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케이비사이언스
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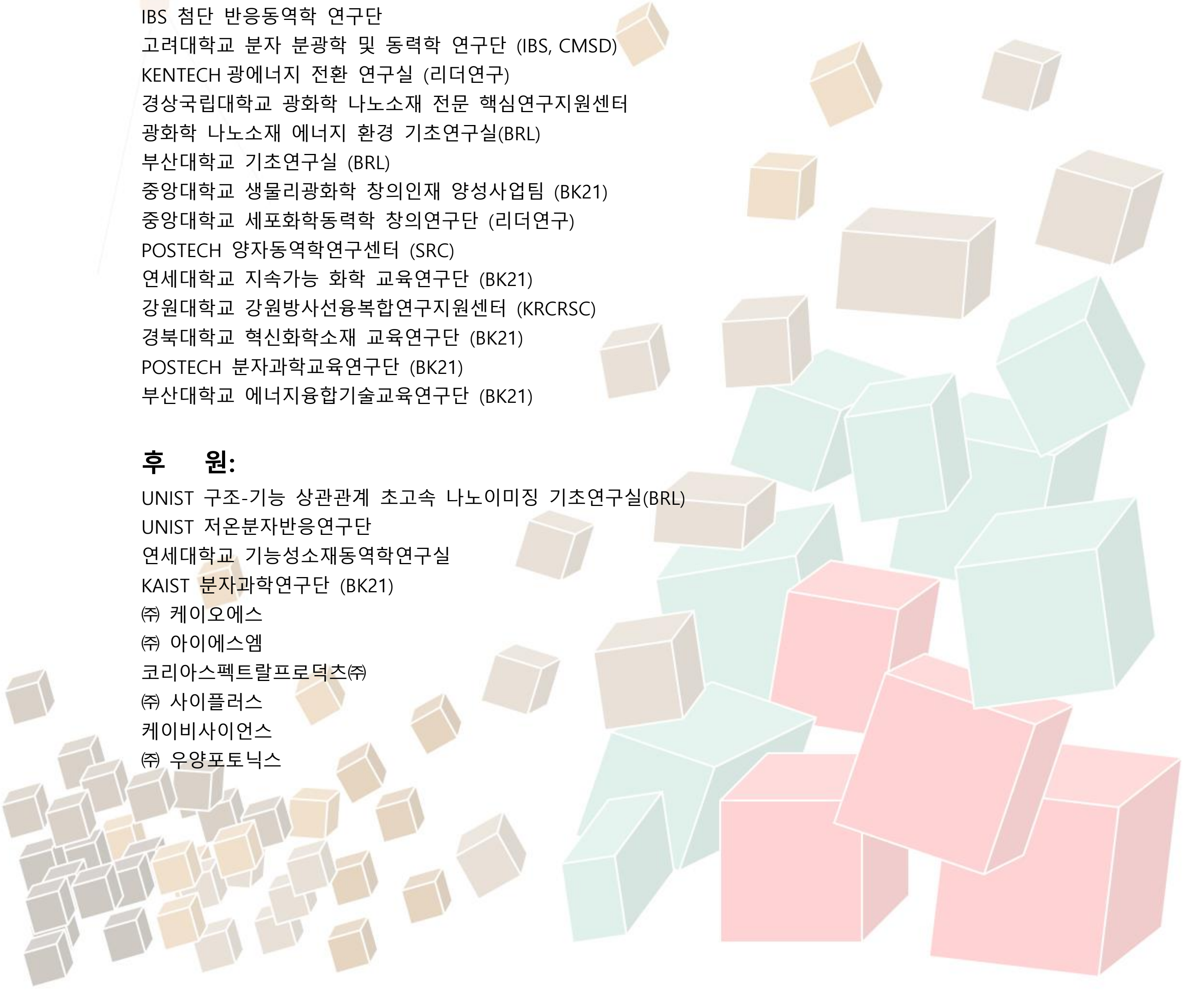

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Date Time	June 18th (Sun)	June 19th (Mon)	June 20th (Tue)	June 21st (Wed)
AM 9:00 10:00 11:00 12:00 PM 1:00 2:00 3:00 4:00 5:00 6:00	Discussion	Committee meeting Registration Opening Remarks Symposium 1 Coffee Break Symposium 2 Poster Session 1 Drawing Lots	Registration Symposium 3 Coffee Break Symposium 4 Group Photo Lunch Poster Session 2 Coffee Break Symposium 5 Award Ceremony/ Drawing Lots Banquet	Registration Symposium 6 Coffee Break Symposium 7 Drawing Lots Closing Remarks

제140차 대한화학회 물리화학분과 여름 심포지엄

학술 발표 프로그램

6월 18일 (일요일)	
토론 세션 좌장: 곽경원 교수 (고려대학교)	
13:00 – 18:00	물리화학 분과 발전을 위한 토의

6월 19일 (월요일)	
09:30 – 12:00	준비 회의
13:30 – 13:40	개회사: 분과회장 강영수 교수 (한국에너지공과대학 에너지공학부)
심포지엄 1 좌장: 김태우 교수 (국립목포대학교)	
13:40 – 14:05	박명기 교수 (국립부경대학교 화학과) Raman Studies on Hybrid Organic–inorganic Perovskite Quantum Dots Using Ultra-low Frequency Raman Spectroscopy
14:05 – 14:30	이승준 (한국교통대학교 교통에너지융합학과) Laser Assisted Synthesis of Nanomaterials and their Applications in Sustainable Energy and Environment
14:30 – 14:55	김남준 교수 (충북대학교 화학과) Electronic circular dichroism spectroscopy of chiral molecules and ions in the gas phase
14:55 – 15:10	Coffee Break
심포지엄 2 좌장: 김경환 교수 (POSTECH)	
15:10 – 15:35	이상진 (IBS) Investigating light-induced structural dynamics of bacteriophytochrome using time-resolved X-ray liquidography
15:35 – 16:00	허준 (IBS) Visualizing the structure and photodynamics of ion in solution using time-resolved X-ray liquidography
포스터 1 (P-1~P-58) 좌장: 곽경원 교수 (고려대학교)	
16:00 – 17:40	포스터
17:40 – 18:00	경품 추첨

6월 20일 (화요일)

심포지엄 3 좌장: 박재우 교수 (충북대)	
09:30 – 09:55	장준경 교수 (부산대학교 나노융합기술학과) Molecular Features and Surface Wettability of an Interfacial Water
09:55 – 10:20	이상욱 (성균관대학교 화학공학과) Strategic Catalyst Design and DFT-based Simulation Method Study
10:20 – 10:45	정재훈 교수 (울산대학교 나노에너지화학과) Computational insights into molecular behaviors on solid surfaces
10:45 – 11:05	Coffee Break
심포지엄 4 좌장: 최명룡 교수 (경상국립대)	
11:05 – 11:30	김태규 교수 (연세대학교 화학과) Femtosecond UV Photochemistry of the L-cysteine Disulfide Moiety in Solution by Time-Resolved X-ray Spectroscopy
11:30 – 11:55	최정권 (IBS) Singlet Fission Dynamics Modulated by Molecular Configuration in Covalently Linked Pyrene Dimers
11:55 – 12:30	주태하 교수 (POSTECH 화학과) Dynamics of Excited States by Time-Resolved Spectroscopies and Molecular Dynamics Simulations
12:30 – 12:40	Group Photo
12:40 – 14:00	Lunch
포스터 2 (P-59~P-115) 좌장: 곽경원 교수 (고려대학교)	
14:00 – 15:40	포스터
15:40 – 16:00	Coffee Break
심포지엄 5 좌장: 강명종 교수 (국립강릉원주대)	
16:00 – 16:25	박정영 교수 (KAIST 화학과) Probing and Utilizing Hot Carriers for Plasmonic Photoelectrochemical Processes
16:25 – 16:50	서현욱 교수 (상명대학교 화학에너지공학과) The role of interfacial Fe-C-Al sites for catalytic CO oxidation over the Fe-oxide nanoparticles supported by mesoporous Al_2O_3
16:50 – 17:15	김정민 (한국에너지공과대학) Concentrated Electrolytes: From Underscreening to Ion Transport
17:15 – 17:40	이동호 교수 (울산대학교 나노에너지화학과) Surface Composition-Dependent Photoelectrochemical Properties of Transition Metal Oxide Semiconductors
17:40 – 18:10	분과 총회 및 시상/ 경품 추첨
18:10 –	Banquet

6월 21일 (수요일)

심포지엄 6 좌장: 이주용 교수 (서울대학교)	
09:30 – 09:55	박성남 교수 (고려대학교 화학과) TBA
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10:20 – 10:45	김우연 교수 (KAIST 화학과) Generative AI for accelerated materials discovery
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11:05 – 11:30	김형민 교수 (국민대학교 응용화학부) Macroscale Raman Imaging for Chemical Analysis
11:30 – 11:55	임종민 교수 (경북대학교 화학과) Adaptive optical coherent Raman scattering microscopy to overcome limitations in penetration depth and sensitivity
11:55 – 12:10	경품 추첨
12:10 – 12:20	폐회사: 분과회장 강영수 교수 (한국에너지공과대학 에너지공학부)

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1-3	Electronic circular dichroism spectroscopy of chiral molecules and ions in the gas phase	김남준 교수 충북대학교 화학과
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심포지엄 3		
3-1	Molecular Features and Surface Wettability of an Interfacial Water	장준경 교수 부산대학교 나노융합기술학과
3-2	Strategic Catalyst Design and DFT-based Simulation Method Study	이상욱 교수 성균관대학교 화학공학과
3-3	Computational insights into molecular behaviors on solid surfaces	정재훈 교수 울산대학교 나노에너지화학과
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4-2	Singlet Fission Dynamics Modulated by Molecular Configuration in Covalently Linked Pyrene Dimers	최정권 박사 IBS
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5-4	Surface Composition-Dependent Photoelectrochemical Properties of Transition Metal Oxide Semiconductors	이동호 교수 울산대학교 나노에너지화학과
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P-87	Mechanistic studies of the conversion of bimetallic NiCo-oxide into NiCo-alloy via a novel pulsed laser irradiation technique	Sagyntay Sarsenov 경상국립대학교
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P-99	Temperature-dependent dioxygen reaction of an organonickel(II) complex	윤초록 KAIST
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P-102	Mechanical force transferred through DNA diblock: Scission of a specific covalent bond	김규린 부경대학교
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P-109	Mechanistic study on N-dealkylation of a Co(II) complex	류우열 KAIST
P-110	Advancements in AI-assisted Reaction Planning	Umit V. Ucak 서울대학교
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P-115	Force Field dependent structural and dynamical properties in lithium/ionic liquid electrolytes	정승원 POSTECH

초청 강연 초록

(1-1)

Raman Studies on Hybrid Organic–inorganic Perovskite Quantum Dots Using Ultra-low Frequency Raman Spectroscopy

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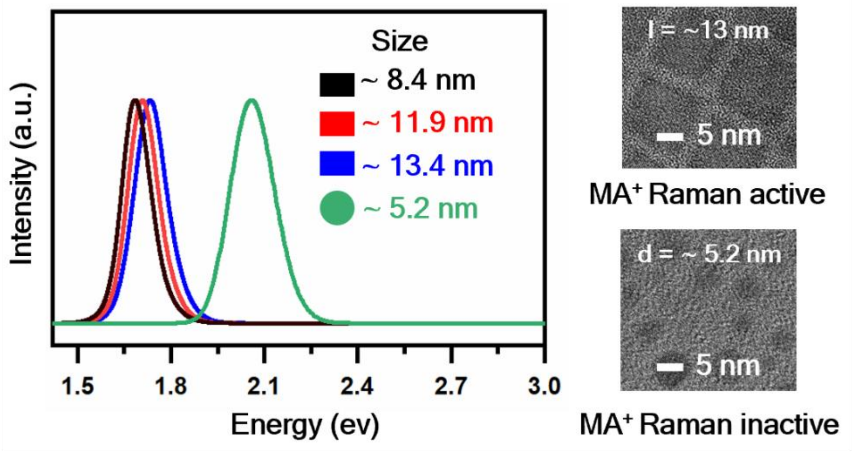
Raman spectroscopy is widely used for chemical analysis due to its ability to provide highly sensitive chemical fingerprints that reflect the structures of analytes. Specifically, for the analysis of halide perovskite materials, ultra-low frequency Raman spectroscopy offers unique insights into slowly oscillating intermolecular vibrations and phonon modes, particularly within organic and inorganic crystalline lattices.

In this seminar, we will present our recent findings on ultra-low frequency Raman spectroscopy of organic-inorganic halide perovskite quantum dots. The materials are methylammonium (MA) and formamidinium (FA) halide perovskite quantum dots, as well as inorganic cesium lead bromide (CsPbBr3) perovskite quantum dots.



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(1-3)

Electronic circular dichroism spectroscopy of chiral molecules and ions in the gas phase

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Circular dichroism (CD) spectroscopy of jet-cooled molecules provides conformation-specific CD spectra. However, its widespread utilization has been limited by the weak CD effects and low density of gas-phase molecules. Here, we developed a dual-beam method to improve the sensitivity and accuracy of gas-phase CD measurements [1]. The resonant two-photon ionization CD spectrum of (1*R*,2*R*)-(–)-pseudoephedrine revealed that the standard deviations of CD values measured using the dual-beam method were three times lower than those measured using a single-beam method. Using the dual-beam technique we obtained the R2PICD spectra of jet-cooled styrene oxide (SO) near the origin band of the S_0-S_1 transition to investigate the effects of vibrational modes on electronic CD values. The IR-UV double resonance spectra showed that SO was present as a single conformer in the jet. The dual-beam R2PICD spectrum of SO exhibited well-resolved vibronic CD bands, of which the signs and magnitudes varied depending on the types of vibrational modes. We will discuss the possibility of using the dual-beam R2PICD spectroscopic technique to determine the absolute configurations of chiral molecules with multiple chiral centers.

The second topic is about the CD spectroscopy of molecular ions produced by electrospray ionization (ESI). We obtained the first CD spectra of chiral molecular ions produced by ESI using cryogenic ion spectroscopy[2]. Protonated L-phenylalanine (L-H^+Phe) and L-phenylalanyl-L-alanine (L-H^+PheAla) ions produced by ESI were stored in a cryogenic quadrupole ion trap and irradiated by multiple laser pulses with left- or right-handed circular polarization. Both L-H^+Phe and L-H^+PheAla were found to exist as two different conformers in the ion trap by infrared IR ion-dip, IR-UV hole burning (HB) and UV-UV HB spectroscopy. The CD spectra of each protonated ion exhibited well-resolved CD bands of the two conformers, whose signs and magnitudes were different from each other. For application of this CD spectroscopic technique to protein ions, we investigated the UV photofragmentation spectra of multiply charged ubiquittin ions, UQ^{+m} (m=6-10), produced by ESI. We will discuss a new technique to measure the conformation-selective UV and IR spectra of UQ^{+m} by introducing two UV laser pulses inside and outside of a cryogenic ion trap as a hole-burning and a probe laser pulse, respectively.

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(2-1)

Investigating light-induced structural dynamics of bacteriophytochrome using time-resolved X-ray liquidography

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Bacteriophytochromes (BphPs) are a significant group of photoreceptor proteins that play a crucial role in regulating various biological processes via the reversible photoconversion between the red-light-absorbing (Pr) and the far-red-light-absorbing (Pfr) states. Structural studies have shown that BphPs adopt a modular architecture where individual domains are connected to an extended helical backbone at the dimer interface. As the input photosensory and output enzymatic domains are spatially separated, it is believed that the activation of BphPs involves long-range structural changes through an allosteric mechanism. Nevertheless, the protein structural dynamics underlying Pr/Pfr photoconversion between the Pfr and Pr states are still elusive. In this study, we employed time-resolved X-ray liquidography (TRXL), also known as time-resolved X-ray solution scattering (TRXSS), to capture global structural transitions activated by the parental Pfr state in a photosensory module of bathy BphP from *Pseudomonas aeruginosa* (PaBphP). From the kinetic analysis of the TRXL data, we identified three distinct structural species, which are attributed to lumi-F, meta-F, and Pr, connected by time constants of 95 μs and 21 ms. Structural analysis based on molecular dynamics (MD) simulations demonstrates that the light activation of PaBphP accompanies quaternary structural rearrangements from an “II”-framed close form of the Pfr state to an “O”-framed open form of the Pr state in terms of the helical backbones. This study provides valuable insights into the mechanism by which modular signaling proteins like BphPs transmit structural signals over long distances, thereby regulating downstream biological responses.

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Visualizing the structure and photodynamics of ion in solution using time-resolved X-ray liquidography

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Energy, structure, and charge are fundamental quantities characterizing a molecule. Whereas the energy flow and structure change in chemical reactions are experimentally characterized, determining the atomic charges of a molecule in solution has been elusive, even for a triatomic molecule such as triiodide ion, I_3^-. Moreover, it remains to be answered how the charge distribution is coupled to the molecular geometry; which I-I bond, if two I-I bonds are unequal, dissociates depending on the electronic state. Here, femtosecond anisotropic x-ray solution scattering allows us to provide the following answers in addition to the overall rich structural dynamics. The analysis unravels that the negative charge of I_3^- is highly localized on the terminal iodine atom forming the longer bond with the central iodine atom, and the shorter I-I bond dissociates in the excited state, whereas the longer one in the ground state. We anticipate that this work may open a new avenue for studying the atomic charge distribution of molecules in solution and taking advantage of orientational information in anisotropic scattering data for solution-phase structural dynamics [1].

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(3-1)

Molecular Features and Surface Wettability of an Interfacial Water

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A hydration layer universally grows on a surface. Such a hydration layer plays a crucial role in various chemical and biologic processes at the interfaces. Significant gaps exist in the current understanding of the molecular structure and dynamics of a hydration layer. We discuss the molecular features of a hydration layer learned from molecular simulation, atomic force microscopy, and vibrational-sum-frequency-generation spectroscopy. An array of pillars is commonly constructed on a surface to control the surface wettability. The wettability of such a pillared surface is quantified by the contact angle (CA) measured for a droplet deposited on the surface. The present theories often fail to reproduce experimental CAs. We present a convolutional neural network model which accurately predicts the experimental CAs.

References

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Strategic Catalyst Design and DFT-based Simulation Method Study

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In recent years, electrocatalytic reactions, such as HER/OER/ORR/NRR/CO2RR/IRR, have attracted substantial interest regarding the development of chemical-electrical energy conversion and storage technologies such as water splitting, fuel cells, rechargeable metal–air batteries, and supercapacitors. Therefore, a wide variety of strategies to develop cost-effective non-precious catalysts with comparable electrocatalytic activities to rare transition metal catalysts have been devised. Here, we introduce our design strategies for catalytic activity on two-dimensional (2D) carbon-based nanomaterials and a novel mineral-inspired catalyst design. In addition, we would like to raise issues of DFT-based simulation methods of electrocatalytic reactions.

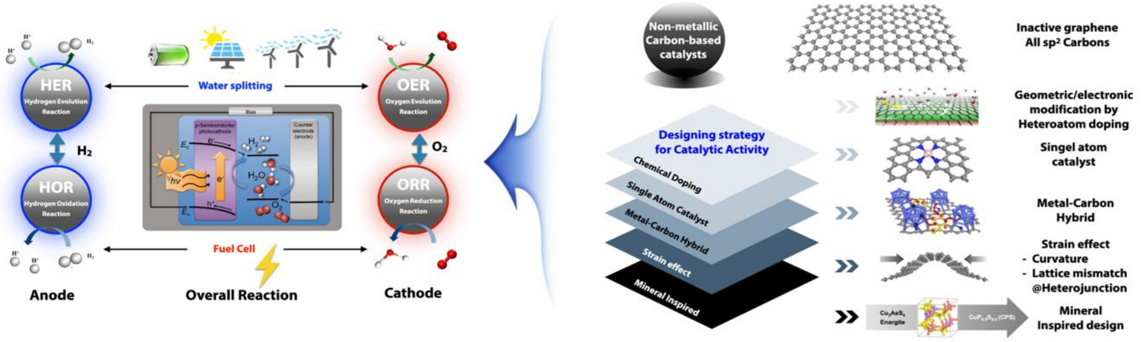

Figure 1. Strategic catalyst design for chemical-electrical energy conversion and storage devices.

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(3-3)

Computational insights into molecular behaviors on solid surfaces

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The molecular behaviors, such as adsorption, diffusion, desorption, and chemical reactions, and their uniform arrangements on solid surfaces are a research topic of great importance not only as a fundamental subject in surface science but also for applications of heterogeneous catalysts, sensors, and molecular-scale electronic devices. Interfacial interaction between molecule and substrate has long served as a key element to achieve robust predictability and high controllability in a variety of applications. Herein, the recent computational investigations, based on density functional theory (DFT), in close conjunction with scanning tunneling microscopy (STM) experiment at atomic spatial resolution provides insights into (i) the two-dimensional chirality created from a coverage-dependent molecular arrangement on metal surface and (ii) the selective molecular diffusion controlled by electric field on ultrathin insulating film. Firstly, four coverage-dependent phases of dehydrobenzo[12]annulene were uniformly fabricated on Ag(111), exhibiting unique chiral characteristics from the single-molecule level to two-dimensional supramolecular assemblies.[1] All coverage-driven phase transitions stem from adsorption-induced *pseudo*-diastereomerism, and our observation of a lemniscate-type (∞) supramolecular configuration clearly reveals a drastic chiral phase transition from an enantiomeric chiral domain to a *meso*-isomeric achiral domain. Secondly, the diffusion direction of naphthalocyanine can be controlled by the sign of electric field between STM tip and ultrathin insulating NaCl film despite the isotropic molecular dipole. The DFT study revealed that the diffusion barrier can be altered due to the molecular adsorption structure and the ionic displacement of NaCl film in a controlled manner.

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(4-1)

Femtosecond UV Photochemistry of the L-cysteine Disulfide Moiety in Solution by Time-Resolved X-ray Spectroscopy

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The disulfide bond is one of the most important structure-making moieties in proteins, stabilizing the latter's tertiary structure when two spatially adjacent L-cysteinyl form a covalent disulfide bond – the disulfide bridge. In aliphatic disulfides, the emergence of several photoproducts after UV irradiation has been reported over the past five decades, the formation mechanism and yields of which are still controversial. Time-resolved X-ray absorption spectroscopy (TR-XAS) is uniquely positioned to identify with high chemical specificity the nature of the earliest photoproducts by probing the sulfur core-level transitions. We demonstrated that TR-XAS at the S K-edge is a chemically sensitive tool to observe the UV photochemistry of small organosulfur compounds in nonpolar solvents [1, 2]. We investigated the natural amino acid dimer L-cystine in aqueous solution and also performed the same experiments in a tripeptide dimer bound by a disulfide bridge (glutathione disulfide, GSSG) in a bottom-up approach to find that L-cystine already captures the essence of the ultrafast photochemistry of the disulfide bridge in aliphatic disulfides. We conclude that upon 267 nm irradiation, aliphatic disulfides in aqueous solution immediately and exclusively undergo homolytic bond cleavage leading to the formation of two identical radicals. The subsequent geminate recombination of the thiyl radicals at ~3eV above the L-cystine ground state occurs with a time constant of ~600 fs, resulting in the formation of a secondary product on the L-cystine ground-state potential energy surface. We attribute the secondary reaction to perthiyl radical generation, a process only possible in condensed phases. We believe that we have conclusive evidence to the long-debated perthiyl radical generation mechanism from the first application of femtosecond XAS in the tender X ray regime (2 5 keV) to organic photochemistry in solution [3].

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(4-2)

Singlet Fission Dynamics Modulated by Molecular Configuration in Covalently Linked Pyrene Dimers

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Covalently linked dimers (CLDs) and their structural isomers have attracted much attention as potential materials for improving power conversion efficiencies through singlet fission (SF) [1-3]. Here, we designed and synthesized two covalently *ortho*-linked pyrene (Py) dimers, *anti*- and *syn*-1,2-di(pyrenyl)benzene (*Anti*-DPyB and *Syn*-DPyB, respectively), and investigated the effect of molecular configuration on SF dynamics using steady-state and time-resolved spectroscopies [4]. Both *Anti*-DPyB and *Syn*-DPyB, which have different Py-stacking configurations, form excimers, which then relax to the correlated triplet pair ((T_1T_1)) state, indicating the occurrence of SF. Unlike previous studies where the excimer formation inhibited an SF process, the (T_1T_1)'s of *Anti*-DPyB and *Syn*-DPyB are formed through the excimer state. The dissociation of (T_1T_1)'s to $2T_1$ in *Anti*-DPyB is more favorable than in *Syn*-DPyB. Our results showcase that the molecular configuration of a CLD plays an important role in SF dynamics.

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(4-3)

Dynamics of Excited States by Time-Resolved Spectroscopies and Molecular Dynamics Simulations

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Following photoexcitation to an electronically excited state, a molecule undergoes various processes, including internal conversion, intersystem crossing, and chemical reactions. These dynamics are central to molecular spectroscopy and have significant implications for applications such as solar energy conversion, organic light-emitting diodes, and photosensors. Time-resolved spectroscopic techniques such as time-resolved fluorescence and transient absorption are employed to experimentally investigate these dynamics. While the potential energy surfaces (PESs) with the Born-Oppenheimer approximations are used to study dynamics in low-lying excited states, dynamics in higher excited states require consideration of the non-adiabatic dynamics and the coupling between electronic and nuclear degrees of freedom and the quantum effects like conical intersection.

For studying early-time dynamics using time-domain spectroscopy, ultrashort ~10 fs pulses are utilized. Nuclear wave packets (NWPs) in the initial excited electronic state and the ground state are created by the short-pulse excitation. The NWPs in the excited state are then carried over to product states, while some NWPs orthogonal to the reaction coordinate remain unaffected [1]. The amplitudes, frequencies, and phases of NWPs coupled with the process undergo modifications during the reaction [2]. NWPs may also exhibit non-Condon effects (Herzberg-Teller coupling), providing insights into the molecular dynamics of the process [3].

To explore the dynamics of molecules undergoing ultrafast internal conversion, intersystem crossing, and chemical reactions in the excited state, we recorded transient absorption and time-resolved fluorescence with high enough time-resolution enabling acquisition of the NWPs. Quantum chemical calculations, quantum mechanics/molecular mechanics (QM/MM) simulations, and nonadiabatic molecular dynamics simulations were performed to comprehend the quantum dynamics in the excited state [4]. We will present several examples of excited state dynamics, including ultrafast internal conversion, intersystem crossing, proton transfer, and charge transfer.

Taiha Joo is a professor in the Chemistry Department at POSTECH, Korea. He has been a faculty member since 1996, following postgraduate work at the University of Chicago and doctoral work at Cornell University's Chemistry Department. Professor Joo is the director of the Center for Quantum Dynamics (SRC center) at POSTECH and a member of the Korean Academy of Science and Technology.

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Probing and Utilizing Hot Carriers for Plasmonic Photoelectrochemical Processes

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The detection of hot electrons and understanding the correlation between hot electron generation and surface phenomena are challenging questions in the surface science and catalysis community. Hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) appears to be correlated with localized surface plasmon resonance. It has been found that the hot electron flux generated under photon absorption and exothermic chemical reaction is the major mediator of energy conversion process [1-2]. In this talk, I introduce the research direction to attempt to detect the surface plasmon driven hot carrier at the nanometer scale by using scanning probe microscopy. To detect and utilize the hot electron flows at the macroscale level, the metal-semiconductor nanodiodes were constructed. At the nanometer scale, we utilized photoconductive atomic force microscopy to observe photoinduced hot electrons on a triangular Au nanoprism on n-type TiO2 under incident light. This is the direct proof of the intrinsic relation between hot electrons and localized surface plasmon resonance. We observed surface plasmon induced hot hole by using the system of Au nanoprism on p-type GaN [3]. I will discuss the impact of hot carriers in the photocatalytic activity under photoelectrochemical water splitting by using Au-based plasmonic nanostructures [4].

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(5-2)

The role of interfacial Fe-C-Al sites for catalytic CO oxidation over the Fe-oxide nanoparticles supported by mesoporous Al_2O_3

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Previously, we demonstrated that Fe-oxide nanoparticles (<~ 3 nm) supported by mesoporous Al_2O_3 can be considered as a potential candidate for the alternatives for Pt-based automobile exhaust gas catalysts, since they can catalyze CO oxidation under low temperature conditions (<~ 100 ^oC) [1]. As a following scientific study, this time, we aimed to get deeper understanding on the origin of catalytic activity of Fe-oxide/Al_2O_3 at low temperature conditions towards CO oxidation. By utilizing various surface-analysis techniques, we managed to reveal the role of interfacial Fe-C-Al sites in low temperature CO oxidation over Fe-oxide/Al_2O_3 catalyst.

Four different Fe-oxide/Al_2O_3, named as 0.5-, 1.0-, 2.0-, and 4.0-Fe, having various amounts of Fe-oxide on mesoporous Al_2O_3 bead were prepared by temperature regulated chemical vapor deposition (tr-CVD) and post-annealing. Their catalytic activities towards CO oxidation under a dry air atmosphere were investigated in the temperature range of 30-350 ^oC, and their surface structures were carefully examined using various surface-analysis techniques (CO-temperature programmed desorption (CO-TPD), CO-temperature programmed reduction (CO-TPR), X-ray photoelectron spectroscopy (XPS), and time of flight-secondary ion mass spectroscopy (ToF-SIMS)).

Under the low temperature conditions (~ 50 ^oC), Fe-oxide/Al_2O_3 sample (0.5-Fe) having the smallest amount of Fe-oxide deposition exhibited the highest activity followed by 1.0-Fe, 2.0-Fe, and 4.0-Fe. On the other hands the activity order of four samples shifted to 2.0-Fe > 1.0-Fe > 0.5-Fe > 4.0-Fe as the reaction temperature increased to 100-150 ^oC. The results of CO-TPD and CO-TPR indicated that the Fe-oxide structures on four Fe-oxide/Al_2O_3 samples (0.5-, 1.0-, 2.0-, and 4.0-Fe) were different qualitatively as well as quantitatively. The XPS and ToF-SIMS analysis results revealed the formation of the interfacial Fe-C-Al species of which population on each Fe-oxide nanoparticle decreased as the amounts of deposited Fe-oxide decreased (0.5-Fe > 2.0-Fe > 4.0-Fe).

Based on our experimental observations, it was suggestive that the Fe-C-Al species can facilitate the low temperature CO oxidation (at 50 ^oC) on the surface of Fe-oxide nanoparticles by activating oxygen atoms. On the other hands, the surface of Fe-oxide nanoparticles can catalyze the CO oxidation without aid of the Fe-C-Al species under higher temperature conditions (> 100 ^oC).

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(5-3)

Concentrated Electrolytes: From Underscreening to Ion Transport

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Electrostatic interactions play a critical role in electrolytes from biological systems to energy materials [1]. The classical Debye-Hückel and mean-field theories provide fundamental understandings of the screening of ionic interactions, but their applicability is limited only to dilute electrolytes. Recent surface force measurement (SFM) experiments [2] have challenged our current understanding of the screening phenomena: various concentrated electrolytes confined by mica surfaces show an unexpectedly long decay length of the force between surfaces (~ 10 nm), referred to as (anomalous) “underscreening.” Furthermore, they exhibit a universal cubic scaling relation, which is still puzzling, of the decay length with ion size after properly normalizing both quantities with Debye screening length. Estimating the decay from the bulk correlation length of the liquids [3,4] has been found not successful enough in rationalizing all the observations in the experiments, resulting in the underestimated exponent of the scaling relation.

This talk discusses our current efforts to understand the microscopic origin of the long decay observed in surface force measurements with concentrated electrolytes, mainly focusing on the effects of confinement and interfaces, which we believe are the missing component in previous theoretical efforts. A grand-canonical simulation method, which we recently developed via a hybrid non-equilibrium MD/MC method [5], allows for the efficient investigation of concentrated electrolytes under confinement in equilibrium with its bulk reservoir as in the SFM experiments. As a first demonstration of our method, I will discuss Donnan equilibrium in a model Lennard-Jones electrolytes in a charged slit-like pore. We found a transition with increasing surface charge density from a Debye-Hückel to an intermediate regime. Nevertheless, the mean excess ion density can still be predicted using the linearized Debye-Hückel theory via an “effective” surface charge density.

Finally, this talk will briefly illustrate how the fundamental understanding of electrostatic interaction screening helps to establish underlying design principles of concentrated polymer-based solid electrolytes. In particular, we suggest a so-called salt-concentrating strategy to develop fast ion-conducting electrolytes with substantial amounts of salt that provide a highway for ion traffic by forming a nanoscale ion-solvation network.

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(5-4)

Surface Composition-Dependent Photoelectrochemical Properties of Transition Metal Oxide Semiconductors

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The utilization of solar energy for the production of chemicals through photoelectrochemical conversion offers a sustainable method to generate high-energy density fuels and address the intermittent nature of sunlight as a power source. Within this system, semiconductor photoelectrodes play a crucial role, and ternary transition metal oxide semiconductors show promise as they are more chemically robust and scalable compared to traditional semiconductors. However, these materials often suffer from poor charge transport properties and significant recombination of electrons and holes. Additionally, the complexity of multinary oxides and the intricate processes involved in photoelectrochemical reactions make it challenging to comprehend the specific effects of composition and structure, particularly at the material's surface, on its photoelectrochemical properties.

This talk focuses on how the surface compositions of ternary oxide semiconductors, specifically bismuth vanadate ($BiVO_4$), can significantly impact their photoelectrochemical properties, even when their surface facets remain identical [1]. A direct comparison was made between Bi-rich and V-rich surfaces of $BiVO_4$. By employing advanced synthesis and characterization techniques, along with theoretical insights, high-quality semiconductor films were first created. These films underwent selective modification of the surface composition, which enabled the capturing of the physical and electronic structure of the interface. The study reveals that enriching the upper atomic layer with bismuth shifts the band edge positions towards the vacuum level, thereby reducing the likelihood of electron-hole recombination at the surface. The composition-dependent interfacial electronic structure was further demonstrated through the preferred dissolution of vanadium (resulting in bismuth enrichment) in $BiVO_4$, leading to enhanced photoelectrochemical performance.

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(6-2)

Protein Structural Properties Prediction from Sequence and Structure using Deep Learning

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‘Structure-function relationship’ is a key concept for studying the biological function of proteins. Thus, characterizing protein structures using experimental techniques such as X-ray crystallography and cryo-EM has been highlighted since the mid of 20th century. However, for some targets, the experiments could not be applied since the target is hard to be crystallized or it is difficult to solve phase. On the other hand, obtaining protein sequences is much easier than solving protein structures. Therefore, the gap between protein structure space and sequence space is increasing.

To fill the discrepancy, in silico modeling of protein structures from sequences is often used. With the help of the recent development of deep learning, AlphaFold from DeepMind showed outstanding performance in predicting protein structures. However, there are spaces to improve, such as secondary structure prediction to help the prediction. Recent advances in protein structure prediction give a hint to use the attention from multiple sequence alignment to get the important information. In this presentation, protein structural property prediction algorithms using deep learning will be introduced. Our method predicts solvent accessible area, secondary structure, and intrinsically disordered region from the amino acid sequence, and drug binding site from the sequence and structure.

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(6-3)

Generative AI for accelerated materials discovery

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Deep learning is attracting great attention for various applications including materials discovery. In particular, generative AI is used to design materials with target properties directly unlike virtual screening that prioritizes pre-constructed candidates according to selection criteria. Here, we first overview representative AI models developed for organic molecule-based molecular design. Then, we propose a building block-based molecular generative AI which designs new molecules with target properties by sequentially adding molecular building blocks to any given starting molecule. A key feature of our model is a high generalization ability in terms of property control and building block types. The former becomes possible by learning the contribution of individual building blocks to the target properties in an auto-regressive manner. For the latter, we used a deep neural network that predicts the bonding probability of two molecules from the embedding vectors of the two molecules as input. The high synthetic accessibility of the generated molecules is implicitly considered while preparing the building block library with the BRICS decomposition method. We show that this model can generate molecules with the simultaneous control of multiple target properties at a high success rate. As a practical application, we demonstrate that the model can be applied to materials design with an example study on drug and OLED design.

References

(7-1)

Macroscale Raman Imaging for Chemical Analysis

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Spontaneous Raman spectroscopy offers several advantages over alternative spectroscopic techniques, but its practical application in the field has been hindered by low sensitivity. One particular limitation is the significant amount of time required to obtain a Raman map of a sample using the raster scan mode. To address this time-detection constraint, we have developed two types of macroscopic Raman systems for applications in the food and environmental sectors. Firstly, we have devised a spatially offset Raman method as a quantitative tool for assessing milk fat composition and detecting toxic chemicals in packaged milk in single detection. By utilizing a line-illumination deep Raman system incorporating both conventional optics and a novel optical fiber probe, we are able to accurately distinguish Raman signals originating from milk fat and those arising from packaging materials. This capability is vital in identifying adulterated milk containing toxic substances, which pose risks to human health, as the toxicity can occur at any stage of production. Secondly, we have introduced a novel one-dimensional hyperspectral Raman imaging technique with macroscopic line illumination. This innovative method enables rapid scanning of large areas at high speeds. Through the implementation of this approach, we have achieved remarkable success in acquiring Raman spectra of microplastics over a 1 cm^2 area with exceptionally fast acquisition times. In conclusion, our developed systems significantly improve the practicality of Raman instruments by addressing the time-detection constraint and enhancing sensitivity.

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(7-2)

Adaptive optical coherent Raman scattering microscopy to overcome limitations in penetration depth and sensitivity

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Coherent Raman scattering imaging is a highly effective way of obtaining chemical information about biomolecules without external labels [1]. However, its ability to image deep tissues is limited by certain factors, such as the intrinsic scattering cross-section and sample-induced aberrations, which results in low image contrast. The presence of complex tissue complicates the issue, as even minor disturbances in the pump and Stokes beam foci can significantly compromise the resolving power of the imaging system.

We have developed a novel approach to address this challenge: a deep-tissue coherent Raman scattering (CRS) microscopy system equipped with advanced adaptive optics (AO). Adaptive optics is a purely optical method that does not harm the sample and offers an ideal solution for deep-tissue CRS imaging. Using wavefront shaping devices such as deformable mirrors and liquid-crystal spatial light modulators (SLMs), AO compensates for aberrations and restores a tightly focused beam in deep tissue [2]. This technique has proven effective in enhancing imaging depth in various nonlinear imaging modalities and is appropriate for CRS microscopy.

Our AO-CRS microscopy system employs a spatial light modulator to correct position-dependent aberrations by measuring the complex tissue aberration caused by elastic backscattering. By implementing this label-free AO-CRS microscopy approach, we have successfully demonstrated vibrational imaging of lipid-rich substances, such as myelin, within the mouse brain, even when imaging through thick and opaque cranial bones. Notably, we achieved a ten-fold enhancement in the pump point spread function (PSF) Strehl ratio, and the image contrast of myelin segments beneath the cranial bone is comparable to that obtained in bare tissue.

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포스터 발표 초록

6 월 19 일(월) : P-1 ~ P-58

6 월 20 일(화) : P-59 ~ P-115

(P-1)

Towards Unknown General Structural Information of Two-Dimensional Glass Transition: A Machine Learning Strategy

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Finding a universal structural origin of glassy dynamics is a challenging problem in the field of the glass transition. Here, we introduce convolutional neural network (CNN) machine learning strategies to shed light on finding a general but still hidden structural origin of two-dimensional (2D) glass transition. The 2D colloidal system is an excellent platform for studying glass transition because one can easily compare the hexatic medium-range crystalline order (MRCO) of a system, which exists in polydisperse colloidal glasses (PC glasses) but lacks in binary colloidal glasses (BC glasses). We find that when the snapshot images of 2D colloidal systems (which only contain structural information) are provided as input data to the CNN machine learnings, they can classify images into liquids and glasses completely. Moreover, the CNN machine learnings trained with BC system (without hexatic MRCO) can also classify PC system (with hexatic MRCO), thus indicating that the hexatic MRCO would not be the structural origin of 2D colloidal systems and there should be another structural information that highly correlates with 2D glass transition besides hexatic MRCO.

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(P-2)

Improving Efficiency of Quantum Chemical Computations through Orbital Space Segmentation

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Quantum chemical calculations for large-scale systems have become increasingly important in recent years. However, advanced computational methods that are relatively accurate are only applicable to small systems due to their high computational cost. Embedding methods were developed to solve the cost problem of large systems for efficient computation. A small but important part of the system, the active site, is computed with a high-level quantum method, while the rest of the system, the environment, is computed with a low-level method. Therefore, it is less computationally expensive than using the high-level method for the whole system, but the accuracy is higher than using the low-level method for the whole system. However, determining the active site of a system is a challenging problem. In other words, it is not straightforward where to apply high-level methods to obtain accurate results. There are many ways to identify active sites, but most methods require hyperparameters such as the number of atoms in active sites that need to be intuitively set. In this study, we introduce an efficient approach to automatically determine the active site by calculating the influence of each atomic or molecular orbital on the overall reaction energy and using it as a criterion to define the active site.

References

(P-3)

Spatial inhomogeneity and molecular aggregation behavior in aqueous binary liquid mixtures

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Solute molecules are completely hydrated in dilute aqueous solutions, but they tend to exhibit aggregation behavior as concentration increases. [1-3] We performed MD simulation with graph theoretical analysis and calculated *h* value in various binary aqueous mixtures to demonstrate bifurcating molecular aggregation pattern [4]. Three cosolvents, that is, methanol, n-butanol, and dichloromethane (DCM), which have different miscibility in water, are chosen. Spatial inhomogeneity analysis shows that miscible methanol solution has low *h* value, meaning homogeneous distribution of given molecules, whereas immiscible DCM mixture has high *h* value, indicating localization of aggregates. In case of butanol-water mixture, it shows temperature dependence in *h* value, which represents phase transition behavior with increasing temperature. In graph theoretical analysis, self-associated or spatially extended aggregation behavior was distinguished. Methanol causes formation of spatially extended aggregates, which are well intertwined with water H-bond network, thus resulting in small *h* value. On the other hand, self-associated aggregates, which are separated from water phase, facilitate phase separation in DCM-water mixture. The spatial inhomogeneity analysis and bifurcating aggregation hypothesis provide crucial clue to understand the fundamental issues, such as miscibility or liquid-liquid phase separation in binary liquid mixtures.

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(P-4)

Temperature Effects on the Phase Behavior and Aggregation Phenomena in aqueous binary liquid mixtures

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Liquid-liquid phase separation is a significant phenomenon observed across a wide range of molecular systems. Recently, we found in use of MD simulation studies that the molecular aggregation affects miscibility and phase behavior in water-alcohol mixtures. [1,2] Temperature has been shown to be a key factor in modulating aggregation pathway and phase behavior in butanol-water mixture.[3] The triethylamine (TEA) is a partially miscible system that exhibits lower critical solution temperature (LCST) behavior. Above the critical temperature, the aqueous TEA mixture separates into two distinct phases: one rich in TEA and the other in water. In contrast, Tri-iso-propylamine (TIPA), a sterically overcrowded molecule, is completely immiscible in water regardless of temperature. In order to obtain understanding of the temperature-dependent aggregation behavior and solubility of the TEA-water and TIPA-water mixtures at a molecular level, we employed a synergistic approach involving MD simulation and graph theoretical analysis along with spatial inhomogeneity analysis.[4] It was shown in this work how temperature affects molecular aggregation and the water network structure in the presence of TEA aggregates. Furthermore, we examined the molecular aggregation behavior to show distinct miscibility in TEA-water and TIPA-water mixtures.

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(P-5)

Photochemistry of Thymine in Solution and DNA Revealed by an Electrostatic Embedding QM/MM Combined with Mixed-Reference Spin-Flip TDDFT

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The photochemistry of nucleobases, important for their role as building blocks of DNA, is largely affected by the electrostatic environment in which they are soaked. For example, despite the numerous studies of thymine in solution and DNA, there is still a debate on the photochemical deactivation pathways after UV absorption. Many theoretical models are oversimplified due to the lack of computationally accurate and efficient electronic structure methodologies that capture excited state electron correlation effects when nucleobases are embedded in large electrostatic media. Here, we combine mixed-reference spin-flip time-dependent density functional theory (MRSF-TDDFT) with electrostatic embedding QM/MM using electrostatic potential fittingfitted (ESPF) atomic charges, as a strategy to accurately and efficiently describe the electronic structure of chromophores polarized by an electrostatic medium. In particular, we develop analytic expressions for the energy and gradient of MRSF/MM based on the ESPF coupling using atom-centered grids and total charge conservation. We apply this methodology to the study of solvation effects on thymine photochemistry in water and thymine dimers in DNA. In the former, the combination of trajectory surface hopping (TSH) nonadiabatic molecular dynamics (NAMD) with MRSF/MM remarkably revealed accelerated deactivation decay pathways, which is consistent with the experimental decay time of ∼400 fs.[2] The enhanced hopping rate can be explained by the preferential stabilization of corresponding conical interactions due to their increased dipole moments. Structurally, it is a consequence of characteristic methyl puckered geometries near the conical intersection region. For the thymine dimer in B-DNA, we found new photochemical pathways through conical intersections that could explain the formation of cyclobutadiene dimers and 6–4 photoproducts.

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(P-6)

Dynamic heterogeneity of water molecules nanoconfined between Zwitterionic Phospholipid Membranes

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Understanding of water behavior confined between biological membranes in nanoscale is crucial to elucidate various biological functions. The interfacial environment between the membrane and water plays a significant role in governing the dynamic properties of nanoconfined water. Despite extensive investigations into the dynamic properties of nanoconfined water, a quantitative understanding of the dynamic heterogeneity of water motion and its relationship with the interfacial environment remains elusive. In this study, we propose a transport equation for nanoconfined water to provide insights into the relationship between dynamic heterogeneity of water motion and the interfacial environment. To validate this theoretical approach, molecular dynamics (MD) simulations were conducted to investigate the transport dynamics of water molecules confined between 1,2-dimyristoyl-sn-glycero-3-phosphorylcholine (DMPC) bilayer membranes with varying the distance between the membranes. Our analysis reveals the existence of an interfacial water region that remains conserved irrespective of the distance between the membrane. Notably, an increase in the proportion of water molecules within the interfacial water region leads to an enhancement of the dynamical heterogeneity of water molecules, while the relaxation time of this heterogeneity decreases. These findings provide fundamental insights for understanding the non-Gaussian transport dynamics of particles in biological nanoconfined spaces.

References

(P-7)

Mechanism of B-Z transition by bending force

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A left-handed double helical structure of DNA, Z-DNA, involves in various biological processes such as transcription regulation and nucleosome positioning. It has been well established that B-to-Z transition occurs under certain circumstances, especially mechanical stresses such as torsion and tension. However, the impact of DNA bending, which is one of the most common type of mechanical stresses, on the formation of Z-DNA is totally elusive. Here, we show that the bending induces the formation of Z-DNA by governing the bending force on DNA via D-shaped DNA nanostructures. We observed the formation of Z-DNA using single-molecule FRET. The midpoint of B-Z transition in methylated DNA was observed around 78 mM $MgCl_2$ in the absence of the bending force, but it dramatically decreased to 2.8 mM, which is physiological salt condition, due to the bending force. According to Monte Carlo simulation, B-Z transition may release the bending stress via the base extrusion at the B-Z junction. Our results obviously show that DNA bending facilitates Z-DNA formation and suggest a new insight into the B-Z transition.

References

(P-8)

Ultrafast Excited State Equilibrium and GFP Chromophore Fluorescence

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My research interests focus on exploring the excited state molecular dynamics and the development of computational methodologies.

The green fluorescent protein (GFP) exhibiting bright green fluorescence when exposed to UV light,[1] has been extensively employed in cell biology, physiology, and medicine as a useful fluorescence probe. It is widely accepted that the protein environment makes it fluorescent since the fluorescence is completely lost in a vacuum or solution when the native chromophore is taken out of GFP. In the present work, the nature of intrinsic HBDI− fluorescence was explored with the help of NAMD in combination with the recently developed mixed-reference spin-flip time-dependent density functional theory (MRSF-TDDFT, or MRSF for brevity). The potential energy surface of MRSF gives a good agreement with high level theory (XMS-CASPT2), indicating that NAMD done by MRSF correctly describe excited state dynamics. According to NAMD simulation, the S1 population monotonically decays to the S0 state (the ground state recovery of 43%) at 5 ps of the overall population which is quantitatively in good agreement with the results of action spectroscopy (50 %). Within 100 fs, the molecule remained in a near-planar conformation, indicating that the initial vibrational mode of bond length alternation. After 250 fs, majority of trajectories undergo P twisting while only few of trajectories undergo I-twisting. This P-twisting is mostly accessed from the planar structure due to the almost flat barrier. However, the S1 → S0 population transfer through $CI_{10,\,P}$ were rarely observed due to high energy barrier. Instead, the population is reflected back through a planar minimum and finally reach low energy $CI_{10,\,I}$ for ground state recovery.Using the NAMD trajectories, time-resolved photoelectron spectrum (TRPES) and time-resolved fluorescence spectrum were generated. By comparing simulated spectrum and experimental spectrum, we were able to correctly analyze excited state dynamics and assign experimental lifetimes.

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(P-9)

Stabilizing a Nickel-Rich Layered Oxide Cathode by Doping Zr or Mo for Lithium-Ion Batteries: A First-Principles Study

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The presenting author got his Ph.D. degree from the Department of Nano Fusion Technology, Pusan National University. Currently, he is working as a postdoctoral researcher at the Pusan National University focusing on developing new energy materials for next-generation batteries.

Lithium-ion batteries (LIBs) have attracted tremendous interest due to their excellent performances in electric vehicles (EVs), power grids, and energy storage systems. However, the increasing energy demand requires improved LIBs with higher energy and power density, longer lifetime, and lower cost. Among various parts, the cathode material essentially controls the performance and cost of a LIB.[1] Over the last two decades, extensive research has been carried out to develop a new class of mixed transition metal oxides with the general formula of $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM).[2] The Ni-rich layered oxides have shown promising performances as potential cathode materials in lithium-ion batteries (LIBs). However, the cathode materials with Ni content over 80% have limited applications due to rapid capacity fading and poor rate performance.[3] Lattice doping can improve the structural stability and electrochemical performance of Ni-rich cathode materials.[4] In this work, we perform first-principles calculations to study the effect of zirconium (+4) and molybdenum (+6) doping on $LiNi_{0.89}Co_{0.055}Mn_{0.055}O_2$ (NCM-89).[5] The extensive studies of the projected density of states and magnetic structure show that the high-valence cation doping increases the number of Ni^{2+} ions in the NCM-89. Our atomistic studies suggest that doping can constrain the TM−O slabs by strong Zr−O and Mo-O bonds and prevent oxygen release by reducing the Jahn–Teller active Ni^{3+}s. The Zr- or Mo-doping can also suppress the layered to spinel phase transition of NCM-89 by hindering the Ni^{2+} migration. Our DFT study shows that the Ni ions, together with Co ions at the final stage of delithiation, governed the electrochemical activity of the NCM-89 materials.

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(P-10)

DFT calculation for the PVP-induced CO_2 activation and reduction for the first one-electron transfer of the CO_2RR

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Cu–Sn bimetallic catalyst has garnered significant attention for efficiently promoting the CO_2 reduction reaction (CO_2RR), because of its band energy suitable for large-scale CO_2RR-based hydrocarbon production. However, Cu–Sn alloys have some limitations in producing liquid solar fuels such as formaldehyde, methanol, and ethanol because they lack the ability to sequentially transport multiple electrons/protons through distinct pathways in a different opposite direction. To this end, we developed multifunctional hybrid composite $Cu/Cu_{10}Sn_3$/poly(4-vinylpyridine)/reduced-graphene-oxide/Nafion cathodes for the photoelectrochemical CO_2RR to produce liquid solar fuels with high faradaic efficiency (~72.38%) and solar-to-fuel conversion (~1.702%) for yielding formaldehyde as the main C1/C2 liquid fuel. We also proposed CO_2RR reduction mechanism/pathway for the formation of liquid fuels and found out that the presence of Poly(4-vinylpyridine) (PVP), which has N-heterocyclic pyridinium functional groups in the hybrid composite cathode, reduced the activation and reduction overpotentials of the CO_2RR through the activation of CO_2 molecules in the reactant state, which also reduce the activation energy by increasing the thermodynamic energy level of CO_2 molecules in the reactant state and concurrently lowering the transition-state energy level of the $[CO_2\text{–}PVP]^{\ddagger}$ complex during the rate-determining first-electron-transfer step.

We carried out DFT calculations using G09 to assess the consistency between the theoretically expected and experimentally measured values for the PVP-induced CO_2 activation and reduction in activation energy, which was the first one-electron transfer process of the CO_2RR that is, the rate-determining step. We used simplified conditions (only CO_2; VP with CO_2 in water). Although it has inherent limitations in accurately reflecting the experimental results stemming from the considerably more complicated conditions of the multilayer $Cu/Cu_{10}Sn_3$ and $Cu/Cu_{10}Sn_3$/rGO/PVP/Nafion dark cathodes in an electrolyte solution of 0.5 M $KHCO_3$ with CO_2, we can explain the role of VP in inducing CO_2 activation and lowering the energy of [TS]*, which eventually reduced the activation energy for the first one-electron transfer reaction and subsequently promoted the CO_2RR. All calculations have been carried out using UB3LYP/6-311+G(d,p) with solution except for [TS]* structures. Optimized structures, molecular orbitals, and energy profile will be presented and compared with the experiments.

Acknowledgement

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(P-11)

Improvement and Applications of Stimulated Raman scattering (SRS) and coherent anti-Stokes Raman scattering (CARS) spectro-microscopy

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Raman spectro-microscopy is a widely used chemical imaging technique for its advantages such as chemical selectivity, non-destructiveness, and label-free modality. To enhance the weak intensity of spontaneous Raman signal, there are two main techniques – stimulated Raman scattering (SRS) and coherent anti-stokes scattering (CARS) spectroscopy – that are involved with pump and Stokes beams. In SRS, the simultaneous incidence of the pump and Stokes frequencies on the sample leads to stimulated excitation of the molecular vibration when the frequency difference aligns with a specific vibrational transition. On the other hand, CARS spectroscopy, which is a nonlinear process, is a result of the four-wave mixing process that produces a newly generated blue-shifted field known as the anti-Stokes wave. Our center, IBS CMSD at Korea University, has been engaged in the investigation and utilization of SRS and CARS, focusing on their enhancement and practical applications. To enhance the spatial resolution in SRS, we incorporated a balanced detection scheme with the spectral focusing method. As for CARS, a subdiffraction-limited point spread function (PSF) of the CARS signal is achieved by combining a spatially compressed pump beam. The improved vibrational spectro-microscopy involves in imaging polymer beads mixture as well as the characterization of lipid and protein distributions in U2OS cells.

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(P-12)

Enhancement of CO_2 photocatalytic reduction with metal atom coordinated nitrogen rich polytriazine

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Artificial photosynthesis is one of the best ways to produce an environmentally clean and renewable energy source. Several photocatalytic materials with improving its performance have been reported since the last several years [1-3]. In the photochemical CO_2 reduction system, fuel production depends upon the nature of photocatalyst. As it is well-known that CO_2 molecules are highly stable due to their linear structure, hence it is difficult to capture CO_2 and reduce it. Hence, to choose appropriate catalyst and modifying it effectively is a highly challenging task. In this work we are going to introduce nitrogen rich polytriazine (NPT) nanosheets for CO_2 reduction application. A one-pot microwave-assisted condensation technique was adapted to fabricate nitrogen rich porous polytriazine nanosheets coordinated with transition and post-transition metal atoms to enhance guest-host interactions, leading to 2D quasi-metal-free porous organic network with high CO_2 capturing capacity. Incorporation of metal atoms into the covalently bonded molecular framework enhances its specific CO_2 adsorption capacity by ~ 50%. Photocatalytic CO_2 reduction reaction overpotential and activation energy calculated by simple Tafel plot and EIS measurement techniques. It is examined that the metal modified NPT nanosheets are responsible for effective photocatalytic CO_2 reduction to useful fuel production such as Formaldehyde, Ethanol and Methanol.

Kew words
CO_2 reduction, polytriazine, CO_2 adsorption, reaction overpotential, activation energy.

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This work was supported by the Leader Project at the Korea Institute of Energy Technology (KENTECH) for Environmental and Climate Technology, funded by the Ministry of Science and ICT through the National Research Foundation of Korea (No. 2020R1A3B3079715).

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(P-13)

Fe&Cu dual single atoms decorated N&S co-doped porous 2D Carbon Nanosheets/1D g-C_3N_4 hollow nanotubes heterojunction composite for enhanced photocatalytic CO_2 reduction into solar liquid fuels

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Artificial photosynthesis i.e. photocatalytic reduction of CO_2 into fuels or valuable chemicals, provides a promising solution to the challenges of global warming and energy supply [1]. The development of an efficient artificial photosynthesis system requires a photocatalyst with a wide absorption range (from UV to near-IR region), high charge separation efficiency, strong redox capability, and high CO_2 capturing and activation ability [2]. Tremendous efforts have been devoted to developing efficient and stable photocatalysts for CO_2 reduction, unfortunately, most of the semiconductor-based photocatalysts are not suitable for the large-scale and continuous flow CO_2 reduction [3]. Thus, the development of an efficient, stable, and cost-effective semiconductor-based photocatalyst for CO_2 reduction is an essential requirement for future large-scale commercialization [4]. The present work reports, the successful synthesis of Fe and Cu dual single atoms decorated N&S co-doped Carbon/g-C_3N_4 composite catalysts (Fe&Cu DSAs/N&S-Carbon/g-CN) by a simple thermal polycondensation followed by impregnation method. The prepared photocatalysts were systematically characterized by using various techniques. The atomic-level local geometric structure of Fe and Cu dual single atoms were investigated by X-ray absorption fine structure spectroscopy (EXAFS). The crystal structure and structural properties were characterized by X-ray diffraction (XRD), attenuated total reflectance-infrared spectroscopy (ATR-IR), and Raman spectroscopy. The optical properties and absorption characteristics of the synthesized photocatalysts were characterized by Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS). The size, shape, and surface morphology of the synthesized photocatalysts were investigated by Field emission-scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). The surface elemental composition and chemical states of the elements were determined by High performance-X ray photoelectron spectroscopy (HR-XPS). Additionally, the life-time of photogenerated charge carriers were investigated by time resolved photoluminescence (TR-PL) and steady state photoluminescence (PL) spectroscopies. The photocatalytic CO_2 reduction reaction (PC CO_2RR) is currently under progress, and the results will be reported in the conference.

Kew words

CO_2 reduction, polytriazine, CO_2 adsorption, reaction overpotential, activation energy.

Acknowledgements

This work was supported by the Leader Project at the Korea Institute of Energy Technology (KENTECH) for Environmental and Climate Technology, funded by the Ministry of Science and ICT through the National Research Foundation of Korea (No. 2020R1A3B3079715).

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(P-14)

Synthesis of Sb:SnO_2@TiO_2 microrods

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Artificial photosynthesis is one of the best ways to produce an environmentally clean and renewable energy source. Several photocatalytic materials with improving its performance have been reported since the last several years [1-3]. In the photochemical CO_2 reduction system, fuel production depends upon the nature of photocatalyst. As it is well-known that CO_2 molecules are highly stable due to their linear structure, hence it is difficult to capture CO_2 and reduce it. Hence, to choose appropriate catalyst and modifying it effectively is a highly challenging task. In this work we are going to introduce nitrogen rich polytriazine (NPT) nanosheets for CO_2 reduction application. A one-pot microwave-assisted condensation technique was adapted to fabricate nitrogen rich porous polytriazine nanosheets coordinated with transition and post-transition metal atoms to enhance guest-host interactions, leading to 2D quasi-metal-free porous organic network with high CO_2 capturing capacity. Incorporation of metal atoms into the covalently bonded molecular framework enhances its specific CO_2 adsorption capacity by ~ 50%. Photocatalytic CO_2 reduction reaction overpotential and activation energy calculated by simple Tafel plot and EIS measurement techniques. It is examined that the metal modified NPT nanosheets are responsible for effective photocatalytic CO_2 reduction to useful fuel production such as Formaldehyde, Ethanol and Methanol.

Kew words
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(P-15)

Highly Selective Solar CO_2 Conversion into Formic Acid in Nickel-Perylene-C_3N_4 Semiconductor Catalysts

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Photocatalytic (PC) CO_2 reduction reaction (CO_2RR) into value-added oxygenated products is one of the most promising and low-cost ways of solving climate warming change and energy crisis simultaneously. The breakthrough of this research field greatly relies on the rational design of high-efficiency catalysts. Specifically, to reach higher selectivity and productivity of oxygenated fuel products, it remains great challenge in controlling both sequential simultaneous multi-electron/proton shuttling. Consequently, a multifunctional nickel-perylene-carbon nitride nanosheet (NS-P-g-C_3N_4-Ni) has been designed and constructed systematically to strengthen the short-distance electron transfer and proton overflow through molecule-level spatial confinement and functionality, in which the perylene part acts as the charge separation to produce electron and hole for water oxidation to produce protons at the same time, the nitrogen-rich carbon nitride part adsorbs and activates CO_2 molecules, and finally the nickel part serves as the electron concentrator and CO_2RR active center, respectively. The molecular-level multifunctional integration accordingly improves the selectivity of oxygenated product formic acid (HCOOH) higher than 90%. Several spectroscopies and X-ray absorption technique were combinedly applied to characterize catalyst structure. Additionally, electrochemical methods and theoretical simulation were conducted to probe and verify the active sites for CO_2RR. In the next step, time-resolved *in situ* FT-IR and Raman spectra will be developed to figure out the formation mechanism of active intermediates through CO_2 radical anions ($^{*}CO_2^{\bullet-}$, $^{*}COOH$ or $^{*}CO_3^{-}$). This work sheds light on the construction of effective sites in photocatalytic CO_2 reduction techniques to produce value-added products with high selectivity and productivity in relatively low cost of continuous flowing methods.

Key words: Nickel single site; g-C_3N_4; photocatalysis; CO_2 reduction; proton overflow; intermediate.

Dr. Prof. Long Yang, working in Kentech as a Brain Pool fellow, has been engaged in photocatalytic chemical reactions and polymer degradation for several years, and dedicated to produce and utilize the clean energy fuels from the sunlight, CO_2 gas and waste plastics. He has published more than 45 papers and patents covering the photocatalysis, polymeric semiconductors, high-performance polyimide and two-photon absorption.

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(P-16)

State-averaged adaptive sampling configuration interaction self-consistent field (SA-ASCI-SCF): Approximate SA-CASSCF-level excited state calculations with large active space

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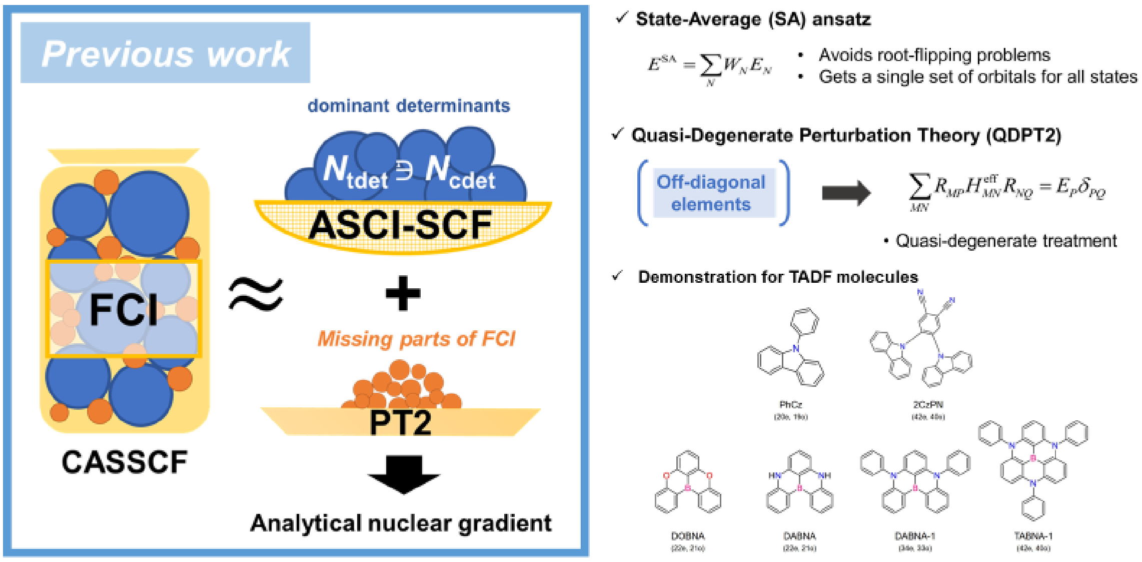
The adaptive sampling configuration interaction (ASCI) method is a deterministic method that approximates the full configuration interaction (FCI) wave function by sampling highly contributing determinants. Based on the ASCI self-consistent field (ASCI-SCF) theory, we have developed an *ab initio* method that approximates state-averaging complete active space self-consistent field (SA-CASSCF) for computing excited states using large active spaces, which is state-averaged ASCI-SCF (SA-ASCI-SCF) theory. To this end, (1) we have introduced a state-average ansatz and quasi-degenerate perturbation theory for excited states with a large active space, and (2) derived and implemented the analytical nuclear gradient for geometry optimization. We have tested the SA-ASCI-SCF method for computing the excited states of carbazole and achieved good agreement with the corresponding SA-CASSCF calculations. We also demonstrate this approach for estimating the singlet-triplet energy gaps and the distributions of radical electrons for various TADF (thermally activated delayed fluorescence) molecules using large active spaces ranging from (20*e*, 19*o*) to (42*e*, 40*o*).



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(P-17)

Study on adsorption mechanism of 1,3-dioxolane on Ge(100) semiconductor surface

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We explored the adsorption structure and mechanism for 1,3-dioxolane on the Ge (100) semiconductor surface by high-resolution photoemission spectroscopy (HRPES) experiments and density functional theory (DFT) calculations. We confirmed that the three peaks in the O 1s core-level spectrum and the four peaks in the C 1s core-level spectrum indicated the two adsorption structures of ring-opening structure and O dative bonded structure. On the basis of DFT calculations, we obtained that the optimized adsorption structures and mechanism of the six possible ring-opening structures through on-top, interdimer row, and intradimer row pathway form O dative bonded structure. In conclusion, we verified that the adsorption of 1,3-dioxolane on the Ge(100) semiconductor surface via the on-top pathway.

References

(P-18)

Adsorption structures of benzothiazole on Ge(100) surface

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We investigated the adsorption configurations of benzothiazole, an aromatic heterocyclic compound, on a Ge(100) using high-resolution photoemission spectroscopy (HRPES) and density functional theory (DFT) calculations. On the basis of the HRPES spectra, we identified two peaks related to positively charged and neutral N atoms in the N 1s core-level spectra. In addition, S 2p core-level spectra showed two peaks related to positively charged and neutral S atoms. This indicates that the adsorption structures of benzothiazole are N dative bonded and S dative bonded structures. Through the DFT calculations, we confirmed the adsorption energies of N dative bonded and S dative bonded structures are -24.48 and -7.99 kcal/mol, respectively, indicating the N dative bonded structure is more stable than the S dative bonded structure.

References

(P-19)

Effect of Au and Pd nanoparticles on the decrease in hydrogen content of zirconium under the pressurized water at high temperature

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One of the main factors that can have a critical effect on the integrity of zirconium alloy cladding during long-term dry storage of spent fuel is the hydride-induced embrittlement by hydride precipitation in cladding. To prevent the degradation of mechanical properties of cladding due to hydride embrittlement, Au and Pd nanoparticles that can absorb hydrogen generated by the reaction between cladding and cooling water [1, 2] are introduced to reduce hydrogen content dissolved in the cladding at the simulated condition of a pressurized water reactor (PWR) with temperature of 315 ℃ and pressure of 15.5 MPa. We investigated the zirconium samples under water at 315 ℃ and 15.5 MPa without and with the addition of Au or Pd nanoparticles. On the basis of X-ray diffraction and Raman results, the change in constitution of zirconium samples from hexagonal Zr to monoclinic ZrO_2 under simulated PWR condition occurred for all the samples, which is caused by the oxidation of zirconium as a result of the reaction with water at high temperature and pressure. In addition, through analytical results obtained from the hydrogen analyzer, we confirmed that the hydrogen content in the zirconium samples under water at 315 ℃ and 15.5 MPa is significantly reduced by Au and Pd nanoparticles.

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(P-20)

Conformer Specific Cryogenic Ion Spectroscopy of Protein Ions in the Gas Phase

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The structure of protein molecules is one of the most popular fields in chemistry. However, the structures and distinguishing of conformers of gaseous cryogenic protein ions are still a mystery. Here, we have obtained the charge state and conformer-specific UV spectra of cryogenic ubiquitin ions produced by electrospray ionization. The nitrogen tagging and dissociation technique was used to record the UV spectra of protein ions. Furthermore, a pump-probe method was used to record the conformer-specific UV spectra. Our study expands the range of the molecules in the cryogenic ion gas phase and opens the way to the cryogenic spectroscopy of huge proteins.

References

(P-21)

Halogen and hydroperoxyl radical formation in polar ice

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In polar regions during springtime, a distinctive photochemical process transforms inactive halide salt ions (such as Br-) into active halogen substances (like Br atoms and BrO). This conversion is linked to the occurrence of ozone depletion events (ODEs) in the polar boundary layer, which are often observed during spring. These events are associated with the amplification of bromine in the boundary layer. The prevailing belief is that the primary outcome of halogen activation is the chemical breakdown of ozone. Additionally, halogens other than bromine, can be activated, although the mechanisms involved are not entirely comprehended.

Using quantum mechanical methods, the formation of XO_2H species (where X = F, Cl, or Br), which are precursors to halogen and hydroperoxyl radicals ($O_2H\cdot$), has been studied. In the case of BrO_2H, the strong spin-orbit coupling (SOC) makes it easy for the initial triplet species to cross over to a more stable singlet species. As a result, the formation of singlet BrO_2H is highly likely, which can then undergo exothermic photo-dissociation to produce $Br\cdot$ and $O_2H\cdot$ radicals (the bright channel). On the other hand, the less energetically preferable, triplet species are weakly bound and can be easily subjected to thermal dissociation, resulting in the formation of $Br\cdot$ and $O_2H\cdot$ (the dark channel). In essence, the bright and dark channels represent two alternative pathways for the formation of $Br\cdot$ and $O_2H\cdot$ radicals.

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References

(P-22)

Reversibility of surface restructuring on Pt-Ni bimetallic nanoparticle under O_2 and H_2 environment

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Bimetallic catalysts are widely used in many catalytic reactions because they exhibit higher catalytic performance than their parent monometallic catalysts [1]. To understand their superior catalytic abilities, investigating their surface is very important. One of their unique properties is surface restructuring. The driving force of adsorbate-induced surface restructuring is the thermodynamic stability of bimetallic surface. In the case of Pt-3d transition metal (3d TM) bimetallic alloys, the Pt-skin is created at the top-most surface under a hydrogen environment because hydrogen molecules are bound more strongly to Pt atoms than 3d TM, whereas 3d TM is present substantially at the surface under an oxygen environment because oxygen molecules adsorb more strongly with 3d TM atoms. Although many observations of formation of Ni oxide under oxidative conditions are reported for Pt-Ni nanoparticles (NPs) [2-3], the research on their reversibility is still required. When going through the redox reaction cycle multiple times, it is important to consider specific factors that could occur on the surface, such as the formation of Pt-skin [4], Pt-Ni alloying [5], and remaining Ni species [6].

In this study, we investigated the surface structure of Pt-Ni NPs under consecutive gas changes from oxygen to hydrogen using ex-situ and in-situ technique. Pt-Ni NPs of random alloy were synthesized via polyol method with polyvinylpyrrolidone (PVP) as a capping agent. Ex-situ X-ray diffraction, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy (XPS) analysis showed that Ni atoms were oxidized and segregated onto the surface under oxygen conditions and re-alloyed with Pt under hydrogen conditions. This phenomenon was confirmed in real time using operando ambient pressure XPS. This study would help to improve the catalytic performance through regeneration of catalysts in industry.

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(P-23)

Theoretical Model for Predicting Mean Free Path of Chemically Excited Hot Electrons on Catalytic Nanodiodes

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Dissipation of chemical energy on the metal surfaces can non-adiabatically generate highly energetic hot electrons. Because of the fast extinction of hot electrons via thermalization, the metal-semiconductor Schottky devices were proposed to directly detect the flow of reaction-induced hot electrons, called chemicurrent. Detection of chemicurrent plays an important role in elucidating mechanisms for charge transfer between the reactant and the catalyst. [1, 2] Despite its importance in determining the catalytic activity, the loss dynamics of hot electrons in catalytic nanodiodes still remain unclear.

Herein, we show a theoretical model that demonstrates the loss mechanisms of hot electrons on catalytic nanodiodes during hydrogen oxidation reactions. The injection efficiency, chemicurrent yield, on Pt/TiO_2 nanodiodes is determined through three steps: generation, emission, and transportation. Hot electrons are generated by the reaction between adsorbed H and OH species on Pt, and their energy distribution is calculated based on the joint densities of states. Then, the emission probability into TiO_2 is determined using the momentum mismatch at the interface. Moreover, the multiple reflections within the Pt layer cause attenuation due to the mean free path (MFP) of hot electrons. By comparing with the experimental chemicurrent yield, our model predicts MFP to be 11 nm, which can offer a more accurate prediction than the previous model suggested by Nienhaus. [3] Furthermore, modeling of the Pt nanoparticles deposited Au/TiO_2 nanodiodes is conducted by additionally considering the trapping in the capping layer. The MFP in Au is calculated as 22~26 nm by controlling the reaction temperature. Based on these results, we expect that our model can provide insights into the understanding of the relation between reaction-induced hot electrons and catalytic activity.

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(P-24)

Investigating the Effects of Surface Plasmon on Capacitance of Metal-Semiconductor Interfaces

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Capacitors are promising energy storage devices with high power and energy densities due to their rapid discharge rates. There is a growing focus on hot electron-based photocatalysts and photoelectric conversion engineering that utilize the surface plasmon effect [1]. In response to this trend, our study aimed to enhance capacitance at the metal-semiconductor interface through the localized surface plasmon resonance effect (LSPR).

In order to achieve this, we performed capacitance measurements under various conditions, including different film structures, light wavelengths and power, and DC bias values. Our results revealed that LSPR can effectively enhance the accumulation and confinement of electrons within the TiO2 layer, resulting in an increase in the real capacitance value. Additionally, we observed that the DC bias and electron diffusion flow influence the imaginary capacitance. The film structure, as well as the wavelength and power of the light, were found to significantly impact the capacitance behavior of the system. Furthermore, the capacitance of the diode was found to be notably affected by the device's surface structure, as well as the wavelength and intensity of the light. Overall, our study provides the broader understanding of charge accumulation during the hot electron generation, with intriguing application of advanced hot-electron based photovoltaic and photoelectrochemical devices.

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(P-25)

Investigation of the Origin of the Enhanced Photoelectrochemical Performance of Gradient W-doped Bismuth Vanadate (BiVO4) photoanodes

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Gradient W-doped Bismuth vanadate ($BiVO_4$) photoanodes were fabricated to figure out the main factor improving the photo-electrochemical (PEC) performance, achieved by the gradient doping. We found that the film in which the concentration of W in the bulk was higher than that in the surface showed the highest photocurrent density, compared to those of other samples, which could be mainly attributed to the improvement of the charge transfer efficiency. It means that W existing on the surface of $BiVO_4$ played a crucial role in the enhancement of the water splitting efficiency and the charge separation achieved by the built-in electric field modestly contributed to the improvement of the performance.

References

(P-26)

Cooperative Effect of Nickel ferrite ($NiFe_2O_4$) Underlayer and Amorphous Nickel Iron Oxide ($NiFeO_x$) Overlayer on the Cathodic Shift of the Onset Potential for Water Oxidation on Hematite (α-Fe_2O_3) Photoanode

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We fabricated a Hematite-based photoanode, treated by both a Nickel ferrite ($NiFe_2O_4$) underlayer and an amorphous Nickel iron oxide ($NiFeO_x$) overlayer, and investigated the effect of the treatments on the photo-electrochemical (PEC) water oxidation.

In this study, we found that introducing the underlayer had a negative effect on the PEC performance, particularly, in terms of onset potential. On the other hand, a cathodic shift could be achieved when the overlayer and underlayer were introduced at the same time, which was larger than that of the single treatment of the overlayer.

We will discuss the origin of cooperative effect of the underlayer and the overlayer on the cathodic shift of the onset potential for water oxidation on hematite photoanode, based on the results obtained by various electrochemical and spectroscopic techniques.

References

(P-27)

Revealing the Roles of Surface Treatments on Hematite (α-Fe_2O_3) Photoanode in the Shift of the Onset Potential

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In this study, we fabricated different types of hematite (α-Fe_2O_3)-based photoanodes, treated with CeO_x, FeOOH, and $NiFeO_x$, and investigated the effect of each treatment on the onset potential shift. We revealed that the hematite films that were treated with either CeO_x or FeOOH on the surface did not exhibit cathodic shifts of the onset potentials in photocurrent density–potential (J–V) curves, in which the significant improvements in charge transfer efficiencies were achieved, while charge separation efficiencies were not significantly enhanced. It means that the enhanced charge transfer efficiency resulting from the catalyzed oxygen evolution reaction did not influence the shift of the turn-on voltage significantly. On the other hand, we were able to observe the significant improvement of the photo-electrochemical performance of hematite treated with $NiFeO_x$, including the cathodic shift of the onset potential, which could be attributed to the enhancement of the charge separation efficiency, resulting from the Fermi level unpinning. It implies that it is necessary to improve the charge separation efficiency rather than the charge transfer efficiency to achieve the low turn-on voltage.

References

(P-28)

Spatiotemporal carrier dynamics of pyrene incorporated multi-cation halide perovskites with enhanced stability

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Multi-cation mixed-halide perovskites, having remarkable optoelectronic properties, are emerging as photoactive layer materials for light-harvesting and light-emitting applicants. Improving the stability of these perovskite materials is the next hurdle for commercialization. Compositional engineering of cation sites and halide ion sites has been proven to improve phase stability. Pyrenes, being a planar conjugated system and a strong electron donor, is anticipated to passivate the defects at grain boundaries. The large size difference should allow the pyrenes to selectively locate in grain boundaries and interconnect the adjected grains through pi-conjugated bridges. This study observed further device stability enhancement by incorporating pyrene molecules in the precursor of $Cs_x(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$ perovskites and spectroscopically unraveled the mechanism behind the improvement. Aided by confocal fluorescence lifetime imaging microscopy (FLIM), the distribution of photoluminescence (PL) lifetime and charge carrier diffusion dynamics were directly visualized in space and time in pyrene-incorporated multi-cation halide perovskites. Pyrene molecules were found to increase the diffusivity rate by a fold of 2 and therefore greatly improve the diffusion length, proving that pyrene molecules assist the charge carrier transport effect by passivating the defects near grain boundaries. We also observed that the addition of pyrene precursors reduces the spatial energetic disorder at the perovskite surface. Furthermore, pyrene molecules Improved the overall stability when exposed to moisture. Perovskite films with pyrene addition showed no degradation in grain morphology and slower formation of nonradiative recombination sites near the grain boundaries.

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(P-29)

Study on valence molecular orbitals of difluoropyridines by high-resolution VUV-MATI mass spectroscopy

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The substitution of a halogen atom in pyridine has garnered the interest of physical chemists due to the reversal of the energy order of molecular orbitals. Furthermore, the characteristics of the highest occupied molecular orbital (HOMO) and the ionization energy in halopyridines are influenced by the substitution positions. This understanding has been derived from previous investigations on 2-fluoropyridine and 3-fluoropyridine, which have demonstrated changes in the stability of the HOMO due to the interaction between nitrogen and fluorine atoms. Building upon this knowledge, our research focused on difluoropyridines to gain a clearer understanding of how fluorine substitution stabilizes the valence orbital with an increasing number of fluorine atoms. In order to achieve this, we investigated the photoionization dynamics of difluoropyridines by utilizing vacuum ultraviolet mass-analyzed threshold ionization (VUV-MATI) spectra, which provide information about the two outermost orbitals of pyridine. This is supported by the Franck-Condon simulations and natural bond orbital analysis.

Hyojung Kim, the presenting author, is a graduate student in master course at the Kangwon National University (Supervisor: Prof. Chan Ho Kwon).

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(P-30)

Determination of conformational stability by IR resonant VUV-MATI mass spectroscopy

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Identifying the conformational structure of a polyatomic molecule is a prerequisite for elucidating the chemical and biological activities of individual conformers. However, deciphering the contribution of each conformation to the vibrational spectrum of the molecule is considerably challenging because the conformers exhibit comparable force fields between their atoms. Therefore, determining the conformational stability still remains a subject of debate. We performed a conformational study of heterocyclic compounds such as THF (C_4H_8O) and morpholine (C_4H_9NO) using the recently developed IR resonant VUV-MATI mass spectroscopy. As a result, it was revealed that for THF in the neutral ground state, the Twisted (C_2) conformer is more stable than the Bent (C_S) conformer by investigating the conformational preferences under various molecular beam conditions. In the case of morpholine, it was concluded that the Chair-Eq conformer is more stable than the Chair-Ax conformer by 108 ± 7 cm^{-1}.

Sung Man Park completed his Ph.D. at Kangwon National University in 2021 under the supervision of Prof. Chan Ho Kwon. He is currently working in the field of Molecular Science and Fusion Technology at Kangwon National University. His research focuses on the study of conformer-specific vibrational spectroscopy of gas-phase molecules.

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(P-31)

Dispersion Corrections to Density-Corrected Density Functional Theory: DC^2-DFT

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Semi-local density functional approximations are often unable to capture long-range dispersion interactions. Various methods have been developed to account for these dispersion forces, among which a posteriori correction approaches are considered beneficial as they retain the computational efficiency of DFT. The recent success of the HF-r2SCAN-DC4[1] is due to its incorporation of dispersion correction as well as the use of Hartree-Fock (HF) density when self-consistent approximate density is inaccurate. In this work, we examine various additive dispersion correction methods including Grimme's dispersion (DFT-D4)[2], the exchange hole dipole moment (XDM)[3], and the many-body dispersion (MBD)[4]. For systematic improvement, the base functional before the correction must be dispersion-less so that the missing interaction can be included separately. When carefully parametrized according to the principles of the density-corrected DFT (DC-DFT), we observed that all three additive correction methods exhibited a quantitatively similar improvement in the dispersion interaction. This outcome remained consistent despite the distinct principles, formulas, and computational speeds associated with each method.

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(P-32)

Theoretical Investigation on the Photochemical Effect of N-B Functionalization of Benzene

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Ultrafast dynamics of organic molecules stimulated by electromagnetic radiation have gained popularity among chemists due to their novelty and broad applicability in the frontier of the chemistry research field. Specifically, aromatic molecules such as benzene have been selected as ideal candidates for investigating photochemical behavior. UV irradiation of benzene yields two possible direct photoproducts: bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene) and tricyclo[3.1.0.02,6]hex-3-ene (benzvalene).[1] However, the photochemical behavior completely changes in the case of B-N functionalized aromatic molecules, such as 1,2-dihydro-1,2-azaborine (referred to as azaborine hereafter). Previous research has reported that UV irradiation at a wavelength of 253.7 nm fully converts azaborine into the Dewar form (2-aza-3-borabicyclo[2.2.0]hex-5-ene),[2] as confirmed by electronic potential energy surface calculations.[3] In this study, we investigate the photoisomerization of azaborine primarily using Tully's surface hopping scheme and compare it with benzene. The results allow us to conclude that atom modification in aromatic molecules can lead to changes in the potential energy surface, and even a small modification can result in a significant alteration of the photoisomerization tendency.

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(P-33)

Surface engineering of core-shell structured Au@Pd nanoparticles decorated on TiO_2 nanotube arrays for enhanced photoelectrochemical oxygen evolution reaction

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Solar light can generate electron-hole pairs and produce photocurrent in the photoelectrochemical system with semiconductors. To utilize the visible light region of the sunlight, metal nanoparticles are attached to the semiconductor and generate hot carriers from metal nanoparticles moving across the Schottky barrier with decreased recombination of electron-hole pairs [1], [2], [3]. To elucidate the effect of the surface composition of bimetallic catalysts on photoelectrochemical reactions, we prepared core-shell structured Au@Pd decorated TiO_2 nanotube arrays (TNAs) with different Pd coverage. Au@Pd/TNAs were analyzed with ultraviolet-visible spectroscopy, inductively coupled plasma mass spectrometry, scanning electron microscopy, and X-ray photoelectron spectroscopy. The photoelectrochemical measurements such as linear sweep voltammetry, chronoamperometry, and incident-photon-to-electron conversion efficiency show that $Au_{30}@Pd_{70}$/TNAs with a sufficient amount of Pd coverage has the highest photocatalytic performance with increased photocurrent. We conclude that controlling the Pd content on the surface of Au nanoparticles can enhance the photoelectrochemical oxygen evolution reaction with increased hot electrons and photocatalytic activity. This work can help to design the surface of the bimetal nanoparticles for efficient photoelectrochemical reactions.

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(P-34)

Dynamics of Photoinduced Electron Transfers in Ir(Ⅲ)-Re(Ⅰ) Photocatalysts

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The conversion of CO_2 to energy-rich compounds using electrons from photocatalysts, after absorbing light, is a promising technology for effectively reducing atmospheric CO_2 and achieving sustainable energy production. In these systems, intramolecular electron transfer (IET) or intermolecular ET between photosensitizer and catalysts are precondition steps for photocatalytic CO_2 reduction. They are crucial for the formation of one-electron-reduced-species (OERS) and for understanding the overall reaction mechanism of CO_2 reduction. Therefore, we have studied the electron transfer (ET) dynamics in a series of Ir(III)-Re(I) photocatalysts, where two bipyridyl ligands of Ir and Re moieties are conjugated at the meta(m) – or para(p) – position of each side. The femtosecond transient absorption (TA) measurements identified the intramolecular electron transfer (IET) dynamics from the Ir to Re moiety, followed by the formation of one-electron-reduced species (OERS) through the intermolecular ET with a sacrificial electron donor (SED). The IET rate depends on the bridging ligand structure, while the formation of OERS occurs on a time scale near 1.4ns. Connecting the Re moiety at the meta-position of the bipyridyl ligands of the Ir moiety induce steric hindrances by restricting the rotational motion around a covalent bond between two bipyridyl ligands. These findings highlight the importance of bridging ligand structures on the ET dynamics in photocatalysts.

Soohwan Kim is a graduate student (candidate for a Master’s degree) in the LAB of Ultrafast Spectroscopy at Korea University under the supervision of Prof. Jae Yoon Shin. He is interested in understanding the chemical reaction dynamics and molecular dynamics occurring in liquid or film phases from a microscopic perspective using various laser spectroscopies.

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(P-35)

Investigating binding affinities of coomasive brilliant blue in protein-dye complex depending on its structural property and environmental pH

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The recent study in the field of cell biology reported that a structural analog of coomasive brilliant blue R (CBB-R) acts as a counter partner against ATP-sensitive purinergic receptors, implying the potential application to a pharmaceutical agent. [1,2] In this study, we focused on investigating the chemical effects of CBB-R dye on the proteins existed in the bloodstream. As a first step, un-natural protein-dye complexes based on bovine hemoglobin (Hb) and serum albumin (BSA) were synthesized by using the low-temperature incubation method. For Hb, the interactions between Hb and CBB-R were examined by varying the environmental pH covering from 6.0 to 8.0. We found that the binding constant (K_a) of Hb-dye complex was maximized at the neutral condition and its binding ratio was 1.5. In contrast, the K_a values in acidic and basic conditions were decreased relative to that in the neutral condition. It is noted that the aggregations of hemoglobin-dye complexes were observed in the entire pH region and it was prominent at the acidic condition. We performed the additional experiments using BSA protein, which has the simpler structure than that of hemoglobin. The characterization of binding affinity for BSA showed that the K_a value was hugely decreased, while its binding ratio was similar to that in Hb. To understand the structural changes in protein-dye complexes, the degrees of secondary structural change were examined by employing circular dichroism spectroscopy. From this measurement, the larger structural change was observed in the Hb-dye complex compared to that in the BSA-dye. The as-synthesized protein-dye complexes will be used for the structural characterization by using temperature-controlled X-ray solution scattering and this approach will provide the structural insight about the underlying mechanism of protein-dyes interaction.

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(P-36)

Structural perturbation from protein-dye interaction revealed by combination of spectroscopies and X-ray solution scattering

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Xanthene dyes have been widely used for cell imaging and bio-molecular analysis in the fields of molecular biology and biochemistry due to its fluorescence property and binding affinity to the biomolecules. [1,2] Despite the active use of xanthene dyes as an external marker, the detailed information about the interaction between protein and dye in terms of protein conformation is elusive. In this study, we aim to reveal the structural interaction on the protein-xanthene dye complexes by using the combination of optical spectroscopies and X-ray solution scattering. As a target system, we prepared the hemoglobin (Hb)-dye complexes by using the xanthene dyes of rhodamine B (RB) and toluidine blue (TB) under the physiological condition of pH 7.2. The binding constants (K_a) and ratio (n) of the dye-protein complexes were determined from the systematic spectroscopic measurements. Our results show that the binding constant between the hemoglobin and dye was directly coupled to the molecular size of the dye. From the circular dichroism spectroscopic measurement, it was found that the smaller size of dye molecule induces the larger conformational change of the complex in view of secondary structure of protein. We also performed the additional structural characterization using small/wide-angle X-ray solution scattering (SAXS/WAXS) in order to understand the overall protein structure, covering from secondary to tertiary structure. [3] Based on this experiment, it was observed that the binding of xanthene dye into the protein matrix causes the entire volume change of the protein conformation compared to the native Hb. This study will provide the direct information about the global conformation for various protein-organic compound complexes in solution phase and it will be an experimental benchmark in the related research fields.

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(P-37)

In-Situ Nanoscale Tribochemical Measurement by Using Electrochemical Atomic Force Microscopy (EC-AFM)

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Recently, it has become very important to understand the influence of environmental factors on nanoscale tribological characteristics because friction, adhesion, and wear tend to depend on environmental and chemical factors such as humidity and functionalization of the surface. In this study, we utilized electrochemical atomic force microscopy (EC-AFM) to investigate tribochemical characteristics of the surface in a voltage-applied electrochemical reaction environment. In order to check whether EC-AFM operates properly, an electrodeposition experiment of copper was conducted by applying a voltage in an aqueous solution of 0.01M $CuSO_4$ + 0.1M H_2SO_4 (pH1) using the frame-annealed gold surface as a working electrode and using platinum wire as a counter electrode and a reference electrode. As a result, a clean gold surface topography could be obtained in an aqueous solution. In addition, copper electrodeposition at -0.6 V (E vs Pt), and stripping at -0.3 V (E vs Pt) were observed. Furthermore, we investigated the tribological properties of the Cu surface and liquid interface in an electrochemical reaction environment using EC-AFM. We discuss the relationship between eletro-tribochemical characteristics, and the topography of the surface while applying the electrostatic potential on the sample.

References

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Plasmonic Au nanogap-controlled core–satellite assembly nanostructure for boosting photocatalytic hydrogen evolution

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Development of photocatalysts highly active in visible-to-near-infrared light region is desired work for the efficient solar energy conversion. Here, we introduce newly designed plasmonic metal–semiconductor hybrid photocatalyst consisting of an Au core–satellite assembly and a crystalline TiO_2 shell. To obtain the core–satellite assemblies, TiO_2 was used as spacer to control the interparticle gaps between the Au nanocrystals. Following the additional growth of TiO_2 and calcination, the Au core–satellite assembly@TiO_2 core–shell nanostructures were successfully synthesized. Depending on a thickness of TiO_2, the gap distance between the core and satellite Au NCs was readily regulated in the same morphological unit. Thanks to this structural controllability, gap distance dependent plasmonic and photocatalytic properties of Au nanocrystal assembly@TiO_2 structures were clearly elucidated. Nanostructures possessing the smallest interparticle distances between the core and satellite Au nanocrystals showed superb photocatalytic performance under the visible-to-near-infrared light irradiation attributed to the strong plasmon coupling between the Au nanocrystals and efficient hot electron transfer from the plasmon coupling site to TiO_2.

References

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Thermodynamic origin of nuclei seed formation and monomer-injection rate dependent crystallization dynamics

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Nucleation and crystallization are of great importance in science and industry. However, thermodynamic origin of stable nucleus seed formation and experimental-condition-dependent crystallization dynamics remain mysteries. Here, we solve these mysteries by presenting the exact size distribution and free energy for a general, microscopic model of nuclei. We show that nucleus seeds have a unimodal size distribution with the most probable size increasing with temperature and total monomer concentration in undersaturation and weak-supersaturation; the nuclei size distribution acquires a divergent tail in strong-supersaturation, causing a phase transition into large crystals. We also investigate chemical dynamics of nuclei seed formation and crystallization under various monomer supply rate, finding that nucleus seeds attain a stable nonequilibrium-steady-state with a monodisperse size distribution when the monomer injection rate is low, but undergo a phase transition to large crystals when the monomer injection rate is above a critical value. Thermodynamic understanding of nucleus seed formation and their crystallization achieved here can be applied or extended to investigate nucleation and phase separation occurring in various complex systems.

References

(P-40)

Resolving the fragile-to-strong transition in water by following temperature-induced structural changes and anisotropy

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Most liquids can be classified into two categories, fragile and strong ones, depending on their temperature dependence of the dynamics. Water at ambient temperature and modest supercooled conditions is considered to be a fragile liquid whereas it is proposed to be a strong liquid at temperatures close to the glass transition, which is 135 K. Thus, it is postulated that there exists a fragile to strong transition somewhere in the deeply supercooled regime. By time-resolved X-ray scattering under Optical Kerr Effect (OKE) condition and evaporative cooling in a vacuum can give a chance to find those properties. For the OKE scattering measurement on supercooled water at PAL-XFEL and other XFELs, we have built the equipment that can generate deeply supercooled water droplets and have successfully tested it down to ~227 K. From the recent experiment at SwissFEL, we have measured temperature induced time-dependent structural changes and OKE relaxation of liquid water down to ~228 K.

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(P-41)

Revealing the structure of benzene-I atom charge transfer complex by time-resolved X-ray solution scattering

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Solvent effects play a crucial role in complex interactions between solvents and molecules during a reaction, influencing the stability of certain intermediate or transient states. In the context of radical alkane halogenation for alkyl halide synthesis, solvent effects have been found to be significant in controlling the selectivity of halogen radicals when reacting with substituted alkanes. Previous studies have demonstrated that the use of benzene and other aromatic hydrocarbons as solvents improves the selectivity of Cl radicals when reacting with tertiary carbons in the photo-chlorination of 2, 3-dimethylbutane. Initially, it was suggested that a η6π-complex forms between the radicals and benzene, but later arguments arose proposing the formation of σ-complexes from these π-complexes. Extensive research has been conducted on benzene-radical complexes based on these two proposals. However, a definitive conclusion has yet to be drawn, and recent DFT calculation studies have indicated the stability of the π-complex. Due to the absence of direct structural evidence from spectroscopic techniques, understanding the structure of the key intermediate that regulates selectivity remains controversial. In this study, we aim to elucidate the structure of the benzene-I atom charge transfer complex using time-resolved X-ray solution scattering.

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Phase and Structure of the Hydration Layer on the Rough Surface Probed by Atomic Force Microscopy

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Structurally ordered layers of water are universally formed on a solid surface in an aqueous solution or under ambient conditions. [1-3] Such a hydration layer significantly affects the wetting of a surface [4-7] and the freezing process involving heterogeneous nucleation. [8] Interestingly, a hydration layer develops not only on a hydrophilic but also on a hydrophobic surface. [9,10]

Atomic force microscopy (AFM) is widely used to probe the molecular structure of a hydration layer. [11] With frequency-modulated AFM one can measure the force on the tip with tens of pN resolution, and the tip-surface distance can be resolved as small as 1Å. [12-14] As an AFM tip approaches a surface within 1nm, the force on the tip typically oscillates with varying the distance between the AFM tip and the surface. [15-17]

To mimic the realistic condition, we modeled the rough surface with waviness and employed the molecular dynamics simulation to investigate how the intrinsic hydration layer formed on a hydrophobic rough carbon surface according to the position of waviness. Furthermore, we examined the effects of the AFM tip on the phase and structure of the hydration layer when it approaches the surface.

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Development of charge carrier-selective heterodyne transient grating spectroscopic technique and its application in the distinction of surface trap states in hematite

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We developed a new spectroscopic technique, which is named the charge carrier-selective heterodyne transient grating (CS-HD-TG) method, for the distinction of surface trap states existing in photocatalysts and photovoltaic materials by employing a burn laser inducing depletion of the number of surface trapped charge carriers. In addition, as a case study, we measured the heterodyne transient grating responses of hematite under bias conditions with and without the burn laser and revealed that two distinct trap states co-exist at the surface of the hematite film and only one of them could act as the reaction intermediate for the oxygen evolution reaction (OER), which is consistent with former studies[1-4].

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(P-44)

Unveiling Fast Electron Transfer Dynamics in Photosensitization Reactions of Zinc Porphyrin Derivatives

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In this study, we have investigated the electron transfer (ET) process of the photosensitization system to understand the complicated multi-electron transfer processes in the photocatalytic system. The Photosensitization ET process occurs in a wide time range, spanning picoseconds to minutes. Although the diffusion rate and slow quenching processes of a series of zinc porphyrin derivatives (ZnPs), which serve as a photosensitizer in the binary hybrid system with a heterogeneous TiO_2/Re(I) for photocatalytic CO_2 reduction, were previously reported, there are not many studies about their fast dynamics. Therefore, we employed picosecond time-resolved fluorescence spectroscopy and femtosecond transient absorption (TA) to investigate the fast ET dynamics under the presence of BIH, the sacrificial electron donor (SED), and TiO_2. As a result, the global analysis of the TA spectra reveals the ET dynamics of the one electron reduced species (OERS) formed at adjacent TiO_2 without involving diffusion. In addition, we found that the quenching process of the ZnPs induced by SED not only occurs via dynamic quenching but also through static quenching as evidenced by the Stern-Volmer analysis of fluorescence lifetimes. In conclusion, designing more efficient photosensitizers for CO_2 conversion requires an accurate understanding of ET mechanisms in the photosensitization reaction. Particularly, for the understanding of these ET mechanisms, ultrafast time-resolved spectroscopy is necessary to unveil the reaction dynamics concealed in steady-state or slow time-resolved measurements.

Taesoo Kim is a graduate student (candidate for a Master's degree) in the LAB of Ultrafast Spectroscopy at Korea University under the supervision of Prof. Jae Yoon Shin. He studies the dynamics of ET in bimetallic photocatalysts, using various time-resolved spectroscopy.

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(P-45)

Accurate Calculation of the Electronic Structure of Two-Dimensional Quantum Dots

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Two-dimensional quantum dots (2DQDs) are one of the most promising platforms for quantum information processing and quantum computing. Computational study of the 2DQD systems require detailed knowledge on the electronic states in the QDs, which can be obtained by solving the Schrödinger equation for the electrons trapped in the QD potential. A popular choice of basis for wavefunctions of the electrons in QDs is the eigenstates of a two-dimensional harmonic oscillator, often referred to as Fock-Darwin (F-D) states. Earlier computational studies of QDs [1] only utilized the ground state F-D state for each QD, which leads to unphysically low tunnel and exchange couplings between the electrons in adjacent dots. Therefore, in order to conduct more quantitative studies of the QD systems, the basis set must be expanded by incorporating higher-lying F-D states. This can be practically accomplished by employing the generating function method [2], a powerful mathematical tool that enables the efficient calculations of one- and two-electron integrals involving higher-order basis states. We show that implementation of the extended basis set in the calculation indeed leads to sufficiently large electronic couplings at realistic QD distances. The computation capability acquired herein can be used for dynamical simulations of QD-based quantum logic gates in the future study.

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(P-46)

Investigating Exciplex and Radical Ion Pair Generation in Peptoid-Conjugated Anthracene-DMA

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The exciplex generated via photo-induced electron transfer (PET) has been studied for decades. However, the entire mechanism has not been fully recognized until recently, and many researchers are working to uncover it. The traditional exciplex system, a mixture of low concentrations of acceptor (A) and high concentrations of donor (D), is complex to analyze because the diffusion of D and A needs to be properly considered, as well as relevant photochemical pathways. Moreover, highly concentrated D may cause unwanted chemical events. To circumvent these issues, a linker between D and A was used, ensuring one-to-one D-A electron transfer and exciplex formation even at low concentrations [1].

In this poster, we developed an exciplex system in which anthracene (An) and N,N-dimethylaniline (DMA) are conjugated on a peptoid scaffold, referring to our previous work [2]. The precise control of the distance and relative orientation between the two conjugated moieties is possible due to the well-defined peptoid helical structure. This system is suitable for researching mechanisms since it does not require a large concentration of donor and does not rely on diffusion to generate exciplex.

Using femtosecond transient absorption (fsTA) and fluorescence upconversion techniques, we examined the excited-state dynamics of the exciplex and the radical anion of An ($\text{An}^{\bullet-}$). It was found that the exciplex and radical ion pairs (RIP) are generated in the peptoid-conjugated An-DMA system in a polar solvent, acetonitrile, on an ultrafast timescale. To obtain the pure kinetics of $\text{An}^{\bullet-}$ and exciplex, the remaining An^{*} spectrum considering the quenched population of An^{*} is obtained with upconversion data, and then it is subtracted from the An-DMA spectrum [3]. The exciplex and $\text{An}^{\bullet-}$ are resolved at 610 nm and 660 nm, respectively in fsTA spectrum. This corresponds to a previous report that suggests the exciplex spectrum is expected to be between those of An^{*} and $\text{An}^{\bullet-}$ because the exciplex is a partially charge-separated species [4].

Different kinetics are observed for two types of peptoid-based exciplex systems: (*i*,*i+2*) with a short distance (4 Å) between D and A in an off-facial orientation, and (*i*,*i*+*3*) with a long distance (6 Å) in a co-facial orientation. The exciplex is formed, and then RIP is generated at the co-facial peptoid (*i*,*i*+*3*). In contrast, the exciplex and RIP are simultaneously observed at the off-facial peptoid (*i*,*i*+*2*). This implies that a twisting motion of the peptoid scaffold makes ultrafast PET possible and converts the exciplex to RIP and *vice versa* on an ultrafast timescale.

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(P-47)

Relativistic Mixed Reference Spin-Flip TDDFT

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The Relativistic Mixed Reference Spin-Flip Time-Dependent Density Functional Theory[1,2] (MRSF-TDDFT), which includes spin-orbit coupling (SOC-MRSF) within the mean-field approximation, has been established[3]. This technique accurately mirrors experimental results for elements such as Carbon (C), Silicon (Si), and Germanium (Ge), and also provides reasonable results for heavier elements like Tin (Sn).

In the SOC computations for the molecule 4-thioThymine, which includes a third-row element, the SOC-MRSF outcomes align well with those from the Spin-Orbit Generalized Multiconfiguration Quasidegenerate second order Perturbation Theory (SO-GMC-QDPT2), irrespective of the geometries and exchange-correlation functionals employed.

This method also predicted an intersystem crossing from S_1 ($n\pi^*$) to T_1 ($\pi\pi^*$) in thymine[2,3], which is composed of second-row elements. Given its consistency and practicality, the SOC-MRSF method seems to be a useful tool for complex situations, such as nonadiabatic molecular dynamics (NAMD), where large systems are involved.

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(P-48)

A New Strategy for Monitoring the Charge Transfer from Perovskite Thin Films to Electron Transport Layers Using a Heterodyne Transient Grating Technique

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We fabricated $CH_3NH_3PbI_3$ ($MAPbI_3$) thin films with and without a ZnO layer and measured the heterodyne transient grating (HD-TG) [1] responses of each film to investigate the charge injection dynamics from $MAPbI_3$ to ZnO, based on the component arising from the recombination of the surface trapped electrons in the ZnO layer with the remaining holes in $MAPbI_3$. In addition, we observed the HD-TG response of the $MAPbI_3$ thin film coated with the ZnO layer in which phenethyl ammonium iodide (PEAI) was inserted between two layers as a passivation layer and confirmed that the charge transfer was enhanced when PEAI existed, based on the increase in the amplitude of the component arising from the recombination and its acceleration.

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(P-49)

Enhancing Catalytic Performance and Hot Electron Generation through Engineering Metal-Oxide and Oxide-Oxide Interfaces

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The interface between catalytic metal and oxide support is an important factor that affects reaction performance [1]. Especially, it is well-known that CeO_2 is an advanced material used as oxide support in oxidation reaction [2] due to high capacity for oxygen storage [3]. However, investigations in combined interfaces of metal-oxide and oxide-oxide at heterogeneous catalysts still have challenges due to their complex structure.

To investigate an impact of both oxide-oxide and metal-oxide interface on methanol oxidation reaction, we chose inverse oxide-metal Schottky nanodiode from the CeO_2/Co_3O_4 nanocubes on Pt film (Fig. 1). CeO_2/Co_3O_4/Pt exhibited higher TOF, partial oxidation selectivity, and chemicurrent yield by a factor of 2, 1.5, and 7, respectively, compared to Co_3O_4/Pt. Furthermore, the CeO_2/Co3O_4 on Pt film showed higher values of both selectivity and chemicurrent yield than CeO_2 on Pt film, indicating that CeO_2/Co3O_4 interface also affects the catalytic reaction. Analyzing the Ce4d and O1s peak of in situ XPS technique, we obtained that the reduction of CeO_2 in CeO_2/Co3O_4/Pt was higher than that in CeO_2/ Pt, and adsorbate oxygen in CeO_2/Co3O_4/Pt was also higher than CeO_2/ Pt under methanol 450 mTorr condition. Therefore, based on these results, we can consider that both oxide-oxide and oxide-metal interface can activate the catalytic reaction but also control the selectivity of the reaction, leading to the enhancement of hot electron flux.

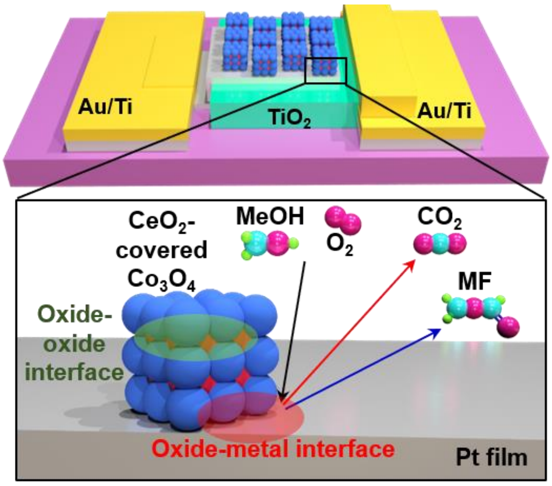

Fig. 1. Methanol oxidation at CeO_2/Co3O_4/Pt film.

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(P-50)

DFT Investigation of Mn(V) Hydroxo Porphyrin-Catalyzed Halogenation of Naphthalene: Mechanistic Insights and Selectivity Analysis

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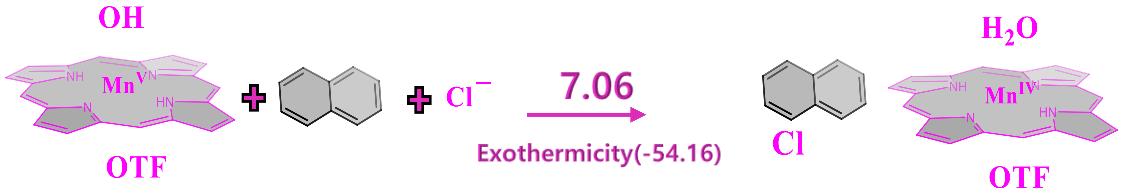
Aromatic halogenation reactions play a crucial role in various fields, including pharmaceuticals, materials science, and agrochemicals. The use of Mn(V) hydroxo porphyrin complexes as catalysts for aromatic halogenation is a promising and versatile approach. However, understanding the underlying mechanisms and factors influencing selectivity is essential for the rational design of efficient catalysts. In this poster presentation, we present a comprehensive study of the Mn(V)-hydroxo porphyrin complex using Density Functional Theory (DFT) calculations to gain insights into its catalytic behavior and selectivity in aromatic halogenation reactions. Through DFT calculations, we investigated the reaction mechanisms and explored the energetics and kinetics of key intermediates and transition states involved in Mn(V)-hydroxo porphyrin-catalyzed aromatic halogenation. Our results provide valuable insights into the regioselectivity and stereoselectivity of the halogenation process, shedding light on the influence of factors such as the hydroxo ligand, electronic properties of the aromatic substrate, and steric effects. The computational investigations revealed the preferred reaction pathways and the role of different factors in determining selectivity, which can guide the design of more efficient catalysts for aromatic halogenation. Additionally, our study explores the potential for alternative reaction pathways and investigates the effects of different reaction parameters on the selectivity of the halogenation reactions.

Scheme 1.



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(P-51)

Searching for the Liquid-Liquid Critical Point in supercooled water with time-resolved X-ray scattering

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Water is the most important liquid for our existence and it has unique anomalous behavior of many of its macroscopic properties. One of the most important topics in physics and chemistry is what causes this anomalous behavior. One major hypothesis is that there could exist two separate macroscopic liquid water phases, high-density liquid (HDL) and low-density liquid (LDL), with a coexistence line in the P-T diagram deep in the supercooled regime at elevated pressure.[1] This liquid-liquid transition (LLT) line is proposed to end in a liquid-liquid critical point (LLCP) and its extension into the one-phase region corresponds to the Widom line.[2] If the LLCP exists in "no-man's land", the discontinuity due to the LLT would disappear at high enough temperatures and only a continuous transition would be observed with a maximum at the Widom line. To investigate supercooled water in the "no-man's land", we measured ultrafast heating from glassy high-density amorphous ice (HDA) state into the HDL and then follow how it transforms to the LDL state (HDA→HDL→LDL). We got direct evidence of LLT from a previous PAL-XFEL beamtime experiment.[3] However, we were not able to obtain high enough temperature jump (T-jump) to reach up to the potential LLCP and Widom line even at the highest base temperature, 115 K. So, the measurements with higher T-jump are desired to observe LLCP experimentally. In this experiment done in PAL-XFEL, we use two lasers to achieve high enough T-jump. A nanosecond laser system (7.29 J/cm2) is used as a pre-heating source and a femtosecond laser system (1.58 J/cm2) is used as a pump for ultrafast T-jump.

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(P-52)

Time-Resolved X-ray Absorption Spectroscopy Reveals the Photo-Homolysis Process of Nickel Complex

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Cross-coupling reactions using nickel catalysts have attracted intense attention in recent years. Specifically, the importance of Ni(I) complexes in the reaction mechanism has been highlighted, as they contribute to a productive Ni(I/III) cycle. However, due to the inherent instability of Ni(I) complexes, various strategies have been explored to facilitate their formation (1). Notably, recent studies have proposed that UV-Vis irradiation of a nickel aryl halide complex can induce aryl homolysis, resulting in the formation of Ni(I) species. Two plausible mechanisms have been suggested: 1) Ni-C bond homolysis occurs from the long-lived lowest excited state (^{3}d-d state). (2) 2) The homolysis occurs via the intersystem crossing between high-energy MLCT state and repulsive excited state (3, 4). While computational and experimental studies have been conducted to elucidate the mechanistic details, the exact mechanism still remains ambiguous. In this study, we measured time-resolved x-ray absorption spectroscopy in picosecond to microsecond time range. We compared the results obtained from two different pump energies, aiming to understand the dynamics of the excited states in the nickel complexes.

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(P-53)

Study of Tyrosine Radical Formation and Di-tyrosine Cross-linking Catalyzed by Transition Metal Ion And H_2O_2 Using Density Functional Theory

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Highly stable and insoluble amyloid plaques in the neuropil cause self-assembled amyloid-β fibril deposition, which is considered to be the cause of Alzheimer's disease(AD). Al-Hilaly *et al.* investigated the formation of di-tyrosine cross-links in the amyloid-β (42) peptide by covalent coupling of two tyrosine residues, which has been implied to play a key role in the development of the Alzheimer's disease [1]. These di-tyrosines can be generated by reactive oxygen species(ROS) catalyzed by transition metal ions such as Cu^{2+}. Using density functional theory, we studied this tyrosine radical formation with transition metal ions such as Fe(II), Cu(II) and H_2O_2 to understand the tyrosine cross-linking mechanism.

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(P-54)

Investigation of Passivating Role of Water Layers on Friction using Ambient Pressure Atomic Force Microscopy

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In tribology, contact between surfaces is essential. Especially in atomic force microscopy(AFM) measurement, friction between tip and sample may vary when material of a tip, environmental conditions, scan speed, and load of a tip. There are many variables in frictional forces, so it is important to restrict the condition to measure friction.

There is discrepancy between experimental condition, which is usually conducted in high vacuum, and environmental condition, which is conducted in ambient condition. This gap is called 'pressure gap', and many people are trying to reduce this gap. In our lab, there is a variable-pressure AFM, which can put various gases inside an AFM chamber and change environmental condition and conduct AFM measurement in that condition [1]. In order to investigate the influence of environmental condition, especially water on the tribological properties, we conducted AFM measurements for friction detection of single crystal Au(111) surface in various humidity conditions : from UHV to 0.1 mbar of water.

At low humidity conditions, relation between friction force versus normal load follows JKR-DMT model. However, when it comes to higher water pressure conditions, friction is reduced at the low load, suggesting the passivating role of water layers and this also can be seen in MD simulation [2]. In **Figure1**, we can observe that as water pressure increases in AFM chamber, friction at 100 nN load decreases. However, when chamber was evacuated to UHV, it returns to a high friction value. Also, at low humidity condition, plastic deformation on Au(111) surface was observed at high normal load(up to 800 nN). However, when it comes to high humidity condition, plastic deformation was not observed due to a reduction of contact stress between a tip and a Au(111) surface. This can be seen in **Figure1.** As pressure of water increases, onset point of plastic deformation increases. When evacuated to UHV, this also returns to its original value.

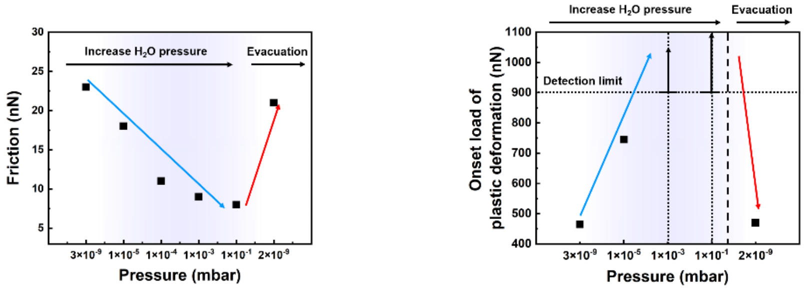

Figure1. Change of friction and onset point of plastic deformation with various humidity conditions.

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(P-55)

Molecular dynamics studies on the polarization effect on Li+ ions diffusion in polyethylene oxide (PEO) electrolytes

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Studying the transport mechanism of Li^+ ions in polyethylene oxide (PEO) melts is critical to developing solid state electrolytes. While computer simulations provided insights on the transport mechanism, simulation studies often ignored polarizability in force fields due to a high computational cost. The polarizability of the molecules may affect the physical properties of Li-polymer electrolyte systems and is known to be caused by the induced dipole moment between Li^+ ions and polymer chains. In order to get insights from the results of molecular dynamics simulations, it is important to know the difference between the simulations with and without the polarizability. This study aims to find out the differences between molecular dynamics simulations with and without polarizability.

In this study, we consider two types of lithium salts (lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium hexafluorophosphate (LiPF6) in PEO melts and perform all-atom molecular dynamics simulations with APPLE&P force field. We employ PEO polymer electrolytes composed of 10 chains of PEO with 54 EO monomers and 54 Li salts (LiTFSI and LiPF6). The APPLE&P force field allows us to turn on and off the polarizability. We find that the polarizability of PEO chains makes Li+ ions bind strongly to the oxygen atoms of the PEO chains with a high coordination number. This result indicates that the polarizability of molecules affects the correlated motion of Li^+ ions and PEO chains. This strong binding slows down the intrachain hopping of Li^+ ions along the PEO chains at short time scales but facilitates the cooperative motion of Li^+ ions with PEO chain segments at intermediate time scales. These findings provide important insights into the development of efficient simulation of polymer electrolyte systems.

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(P-56)

Spectroscopic Studies of O_2 Activation by Organonickel Complexes

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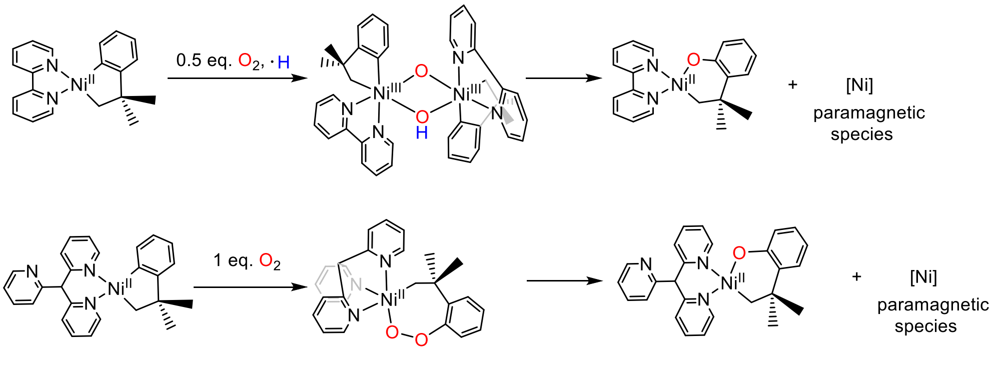
Dioxygen is a powerful oxidant and one of the most frequently used reagents in both nature and industry. However, due to its triplet ground state and strong O-O bond, direct reactions between dioxygen and singlet organic substrates are kinetically challenging. To overcome this difficulty, oxygenases use transition metal active sites, which can reduce O_2 via single electron transfers. Understanding the mechanism of this O_2 activation is important to develop oxygenation catalysts. Previous studies on O_2 activation have mainly focused on copper and iron complexes because they are prevalent in O_2-activating enzymes. Alternatively, aerobic nickel-based oxidation chemistry in nature is limited to few enzymes. Thus, nickel-O_2 chemistry is generally less developed than that of most other 3d transition metals. However, in other previous studies on O_2 activation by nickel, electron-rich ligands or other electron sources have shown to be useful to reduce O_2. Thus, we have chosen organonickel complexes, (bpy)$\mathrm{Ni^{II}(CH_2CMe_2}$-*o*-$\mathrm{C_6H_4)}$ and $\mathrm{(py_3CH)Ni^{II}(CH_2CMe_2}$-*o*-$\mathrm{C_6H_4)}$, which have strong σ-donating alkyl ligands. We have found that these complexes can activate O_2 in an inner-sphere manner as forming oxygenated intermediates. Key intermediates were isolated and their electronic and geometric structures were characterized by employing various spectroscopic techniques such as nuclear magnetic resonance, electronic absorption, and resonance Raman spectroscopies. As a result, a high-valent dinickel intermediate and an organoperoxo Ni intermediate could be defined.



References

(P-57)

Quantitative Analysis of Off-the-shelf Milk using a Line-illumination Raman Probe

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Milk is worldwide consumed product, supplies various nutrients (e.g., Proteins, fats, minerals and vitamins). However, fats from milk can cause increased risk of diseases and also affect obesity development. Accordingly, measuring fat contents of milk is an important issue, and development of its non-destructive and fast analysis method is necessary. Generally, chromatography like GC or LC gives quantitative and qualitative information, but chromatography analysis is expensive, time-consuming, and limited in analysis without opening packaging. That is the reason we select SORS (Spatially Offset Raman Spectroscopy), the most suitable method for analyze without opening package. In this study, we developed method for analyze milk fat without opening package and line-mapping multi-offset Raman Probe system for suppliers, markets and consumers in dairy industry.

References

(P-58)

Observation of Dipole-Bound States with a Triplet Neutral Core using Photofragment Action Spectroscopy

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Observation of dipole-bound states (DBS) with various nitromethane neutral cores (S0, T1, and S1/T2) at the near-threshold region (< 1 eV) and the far-threshold region (1 ~ 4 eV) is presented. Using the photofragment action spectroscopy, the absorption spectrum of DBSs are obtained and well matched with Franck-Condon distributions derived from the anion photoelectron spectrum. Combining photofragment and photodetachment action spectroscopy allows us to explore previously uninvestigated resonances far above the detachment threshold. Additionally, the second band in the photofragment exhibits vibrational structures of triplet neutral state, providing strong evidence for the existence of the triplet DBS. To our current understanding, the experimental observation of triplet DBS is reported for the first time.

We have also investigated clusters of nitromethane anion to gain a deeper understanding of the behavior of nonvalence-bound states (NBS). By the solvent stabilization effect on the anion ground state, the dimer, trimer, and hydrated nitromethane anion exhibit blue-shifted absorption spectra compared to bare nitromethane anion. Absorption spectra of those cluster anions are assigned to NBS absorption, and various reaction pathway from NBS can be revealed by monitoring multiple photofragments. Our experimental findings suggest that not only the NBS near the detachment threshold, but also the NBS far above the threshold can exist and play a role in various reactions, including autodetachment, bond dissociation, and solvent evaporation.

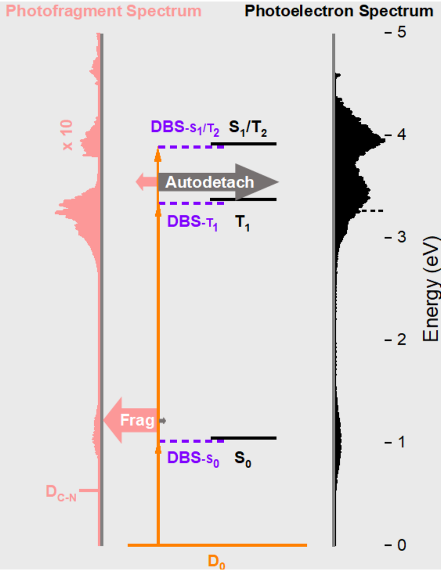

Fig. 1 Photofragment and photoelectron spectra and schematic energy-level diagram of nitromethane anion and neutral states.

References

(P-59)

Rotational Isomerization of Carbon-Carbon Single Bonds in Haloethyl Radicals in Solution

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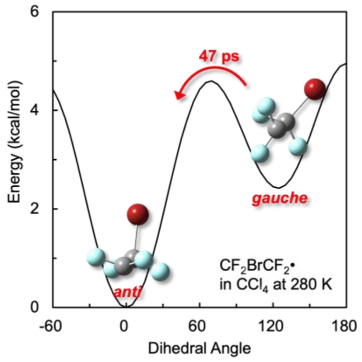
The rotational isomerization of 1,2-disubstituted ethyl radical derivatives, reaction intermediates often found in the reaction of 1,2-disubstituted ethane derivatives, has never been measured because of their short lifetime and ultrafast rotation. However, the rotational time constant is critical for understanding the detailed reaction mechanism involving these radicals, which determine the stereoisomers of compounds produced via the intermediates. Using time-resolved infrared spectroscopy, we found that the CF_2BrCF_2 radical in a CCl_4 solution rotationally isomerizes with a time constant of 47 ± 5 ps at 280 ± 2 K. From this value and the rotational barrier heights of related compounds, CH_3CH_2 and $CH_3CH_2CHCH_3$ radicals in CCl_4 were estimated to rotationally isomerize within 1 ps at 298 K, considerably faster than ethane and *n*-butane, which rotationally isomerize with time constants of 1.8 and 81 ps, respectively. The time constant for the rotational isomerization was similar to that calculated using transition state theory with a transmission coefficient of 0.75.



Rotational isomerization time of the CF_2BrCF_2 radical in a CCl_4 solution at 280 K

References

(P-60)

Density-Corrected DFT for Large Systems: Hartree-Fock Perturbative Correction DFT

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Kohn-Sham Density Functional Theory (KS-DFT) is a widely used method for calculating electronic structures. For most conventional DFT calculations, the density obtained self-consistently is a good approximation to the exact density, but this is not always the case. Recently, HF-r^{2}SCAN-DC4 showed that the DFT energy errors can be reduced significantly by replacing a self-consistently approximated density with the Hartree-Fock (HF) density with the proper dispersion correction (DC4).[1,2] In large systems, however, obtaining HF densities with large basis set is formidable due to high computational cost. HF perturbative correction (HFPC) is an efficient way to calculate HF density at a fairly low cost.[3] In this work, we first demonstrate that the recently developed HF-r2SCAN-DC4 for small molecular systems gives consistently accurate results even for large-scale systems. We also show that, for large systems, HFPC density can be applied to DC-DFT instead of HF density and give quantitatively accurate results at a much lower computational cost.

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(P-61)

First passage time statistics of non-Markovian random walker: Two-state diffusion model

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Analyzing the transport dynamics in complex systems is of great importance due to the many phenomena implemented through transport processes, such as synaptic vesicle trafficking [1] and signal transmission via receptor-G protein interaction [2]. A common behavior observed in various complex systems, including cellular environments, liquid crystals, batteries, and polymers, is the phenomenon where particles diffusing in crowded media exhibit a lower diffusion coefficient than their intrinsic value over long time scales. To describe such behavior, we established a two-state diffusion model where particles undergo state transitions between a bound state following the Ornstein-Uhlenbeck process and an unbound state with a free diffusion. Moreover, when transporting a particle to a desired target point, the first passage time, which represents the time taken to reach the target point for the first time, serves as a crucial metric in target-oriented problems. It also influences the mean squared displacement, which is a key quantity analyzed in the study of diffusion dynamics. We develop an approximation describing the first passage time distribution and moments of displacement over time under a non-Markovian two-state diffusion model. The non-Markovian property of the model has challenges in obtaining the total probability density that incorporates reactions with absorbing boundaries. To overcome this difficulty, we approximated the probability density by several convolutions of the probability density with an absorbing boundary obtained by the Laplace transform and image method. Through this approach, we were able to approximate the first passage time distribution and moments with relatively high accuracy, regardless of the distance to the absorbing boundary. Our research results provide insights for analyzing diffusion dynamics in complex systems by dividing them into detailed diffusion states within the model.

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(P-62)

Enhancing the Photoelectrochemical Performance of $BiVO_4$ Photoanode using Silver Nanoparticles as Effective Photosensitizers

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Photoelectrochemical (PEC) water-splitting is a green approach for generating fuel from solar energy by efficient visible light absorption, as well as separation and transportation of photogenerated charge-carriers. $BiVO_4$ shows great potential in PEC; however, its inadequate light harvesting, and charge separation/transfer limit its performance. Herein, in this study we modified $BiVO_4$ photoanode by introducing active silver nanoparticles (Ag-NPs) to enhance water splitting performance. The Ag-NPs act as efficient photosensitizers, enabling $BiVO_4$ light absorption and charge separation efficiency. In addition, by introducing cobalt phosphate (Co-Pi) as a catalyst for oxygen evolution, improved water oxidation efficiency and stability of photoanode. As a result, $BiVO_4$/Ag-NPs/Co-Pi photoanode demonstrates a improved current density of 4.41 $mA \cdot cm^{-2}$ (1.23 V vs. RHE), almost 5.9-folds greater than pristine $BiVO_4$. The simple surface alteration approach, utilizing noble metal and an oxygen evolution catalyst, improves absorption, charge separation, and transfer efficiency of the photoelectrodes, leading to an enhanced PEC performance.

Keywords: Silver nanoparticles, Bismuth vanadate, Cobalt phosphate, photoelectrochemical water-splitting.

Presenting Author: K. Arun Joshi Reddy, obtained Ph.D. in Chemistry in February 2023 from Yonsei University, presently working as postdoctoral researcher in Chemistry department, Yonsei university, Seoul, Korea.

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(P-63)

Design and Synthesis of a Covalent Organic Framework Bridging CdS Nanoparticles and a Homogeneous Cobalt-Bipyridine Cocatalyst for a Highly Efficient Photocatalytic CO_2 Reduction

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The design and construction of highly efficient photocatalytic CO_2 conversion systems are incredibly desirable for technological, practical, and economic viability. In this study, a 2,2′-bipyridine (bpy)-based ketoenamine covalent organic framework (TpBpy; Tp: 1,3,5-triformylphloroglucinol), which can be prepared on a large scale by a facile and environmentally friendly hydrothermal method, was used to promote CO_2 photoreduction processes by bridging the heterogeneous CdS nanoparticles and a homogeneous $[Co(bpy)_3]^{2+}$ cocatalyst. The bpy units play multiple roles in preparing TpBpy, forming strong interactions with CdS, and accommodating the cocatalyst. In the CO_2 reduction process, due to the flexible association/dissociation between the bpy ligand and the cocatalyst, the active $[Co(bpy)_x]^+$ may separate from heterogeneous CdS/TpBpy and makes space for other unactive $[Co(bpy)_3]^{2+}$ species, thereby maintaining the intrinsic high activity and selectivity of the $[Co(bpy)_3]^{2+}$ cocatalyst. The combination of CdS, TpBpy, and $[Co(bpy)_3]^{2+}$ shows a strong solar light harvesting ability, a high surface area, a high CO_2 adsorption capacity, highly efficient charge carrier transfer at the interface between CdS and TpBpy, and subsequent rapid photoelectron injection into the $[Co(bpy)_3]^{2+}$ cocatalyst. These synergistic effects lead to a robust CO production rate of 35.2 $mmol\cdot g^{-1}$ with 85.0 % selectivity over the first four hours of the reaction. Moreover, the reaction system's quantum efficiencies (AQE) of, with 2 mg of CdS/TpBpy-20%, are 4.75 and 3.65 % at 400 and 450 nm, respectively. Finally, the possible mechanism of the photocatalytic CO_2 conversion over CdS/TpBpy is proposed and discussed here. This study on the heterostructure and photocatalytic system design might serve as a model for the development of solar-driven CO_2 reduction.

References

(P-64)

High-Performance Silver-Doped Porous $CuBi_2O_4$ Photocathode Integrated with NiO Hole-Selective Layer for Improved Photoelectrochemical Water Splitting

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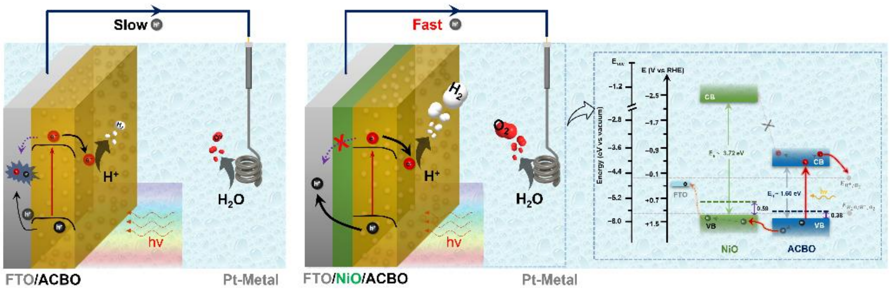
$CuBi_2O_4$ (CBO) has received considerable attention owing to its ideal optical bandgap and positive photocurrent onset potential. However, CBO photocathodes exhibit poor charge carrier separation and transfer across the conducting substrate interface. Herein, a systematic incorporation of Ag^+-cations into nanosized porous CBO network (ACBO) using a simple pulsed-electrodeposition method. In ACBO photocathode, the Ag^+-ions replaced Bi^{3+}-ions, thereby building an increased hole concentration, which further signifies the photogenerated electron–hole separation. Additionally, introducing a low-cost NiO hole-selective layer between ACBO and the conducting substrate enabled a back-interface-aided hole-extraction and electron blocking, resulting in an improved charge transfer across the back interface. Compared with an unmodified CBO, the NiO/ACBO photocathode exhibited a three-fold enhanced photocurrent performance. This enhanced photocurrent originates from the incorporation of a substantial amount of Ag^+-ions into the CBO structure, leading to an increased acceptor density as well as the formation of an appropriate hole-selective layer across the back-contact. The absorption%, time-resolved photoluminescence, and photoelectrochemical impedance spectroscopy measurements unveiled the potential light harvesting, charge separation, and transfer characteristics of the NACBO photoelectrode, respectively. Through this systematic study, we determined an efficient and simple strategy for developing ternary metal oxide-based photocathode/photoanode systems for sustainable energy applications.



Presenting Author: Madhusudana Gopannagari received his M.S. degree in Materials Science and Nanotechnology from Yogi Vemana University (India) and his Ph.D. degree in Chemistry from Yonsei University (South Korea). Currently, he is a post-doctoral fellow at Yonsei University in Prof. Tae Kyu Kim's laboratory. His current research interest includes the synthesis and characterization of new functional materials for photoelectrocatalytic applications and operando photoelectrodes for TR-XAS studies.

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(P-65)

Self-confined oxidation domains in dual metal sulfide catalyst enables active sites for selective photoconversion of Carbon dioxide-to-Methanol by pure water

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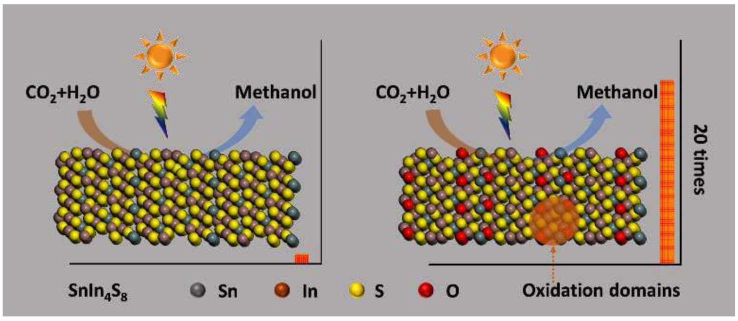
One of the most desirable and challenging research areas is the selective photoreduction of Carbon dioxide (CO_2) to a specific high value-added product such as Methanol (MeOH), which is primarily restricted by poor CO_2 activation and sluggish charge transfer. Herein, we report a facile Hydro-Solvothermal assisted method (HSM) for the construction of precise dual metal site (Sn, In) based photocatalysts. The obtained composites serve as a synergistic catalyst with nearly 100% selectivity for MeOH in pure water under AM1.5 G solar simulator. Formation of a highly stable Sn-C-O-In configuration on dual metal site catalyst ($SnIn_4S_8$) is responsible in promoting the subsequent protonation process for the selective CO_2 reduction to MeOH. Further, the oxidation domains that are confined in the photocatalyst ($SnIn_4S_8$) surface could be self-controlled with Water to Ethylene glycol ratio for the HSM. The experimental and theoretical results indicate that the oxidation domains benefit not only in higher local charge aggregation for the MeOH production, but also in CO_2 adsorption/activation, charge separation, and transportation, resulting in enhanced photoreduction of CO_2 and is twenty times higher than the prismatic $SnIn_4S_8$. This work provides insights into the oxidation domines confined dual metal sulfides on CO_2 photoreduction property, covering the way for higher CO_2 reduction efficiency while retaining the parent catalyst's selectivity. This approach is promisingly generalizable to a wide variety of materials.



Presenting author: Dr. Putta Rangappa is an innovative nanotechnologist and renewable energy enthusiast who is working on designing novel nano heterostructures for photocatalytic applications. He received his PhD degree from Yonsei University's department of Chemistry under Prof. Tae Kyu Kim and is now a postdoctoral researcher in the same lab. His research at present focuses on selective photocatalytic CO_2 reduction processes at neutral conditions utilizing dual metal site-based catalysts.

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(P-66)

Asymmetric Gradient Orbital Interaction of Hetero-Diatomic Active Sites for Promoting C–C Coupling

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Diatomic-site catalysts (DACs) have garnered tremendous attention for selective CO_2 photoreduction, especially in the thermodynamical and kinetical mechanism of CO_2 to C_{2+} products. Herein, we first engineered a novel Zn-porphyrin/RuCu-pincer complex DAC (ZnPor-RuCuDAC). The heteronuclear ZnPor-RuCuDAC exhibit a best acetate selectivity (95.1%), while the homoatomic counterparts (ZnPor-Ru_2DAC and ZnPor-Cu_2DAC) present the best CO selectivity. In-situ spectroscopic reveal that the heteronuclear Ru–Cu sites easily appear C_1 intermediate coupling. The in-depth analyses confirm that due to the strong gradient orbital coupling of Ru4d–Cu3*d* resonance, two formed *CO intermediates of Ru–Cu heteroatom show a significantly weaker electrostatic repulsion for an asymmetric charge distribution, which result from a side-to-side absorption and narrow dihedral angle distortion. Moreover, the strongly overlapped Ru/Cu-*d* and CO molecular orbitals split into bonding and antibonding orbitals easily, resulting in decreasing energy splitting levels of C_1 intermediates. These results can collectively augment the collision probability of the two *CO intermediates on heteronuclear DACs. This work first provides a crucial perspective on the symmetry-forbidden coupling mechanism of C_1 intermediates on diatomic sites.

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(P-67)

Engineering Cu-Site Electronic State on N-Rich Carbon Nitride for Selectivity CO2 Photoreduction

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Atomically monodispersed heterogeneous catalysts with uniform active sites and high atom utilization efficiency are ideal CO_2 photoreduction materials. However, the forceless interactions between catalytic site and CO_2 reduction intermediate restrain the photoactivity and selectivity of CO_2 reduction. Herein, we successfully designed and synthesized Cu diatomic-site catalyst (CuAC) on nanotube-like mesoporous carbon nitride framework (C_3N_5) by using a wet-chemical method, and the obtained CuAC-5 exhibited the best CO yield (329.28 μmol g^{-1} h^{-1}) with 78.8% CO selectivity. To explore the underlying photocatalytic mechanism, the crystal phase, micromorphology, light absorption, energy band structure, element composition, electrochemical behavior and photogenerated electron lifetime of these Cu-containing materials are characterized and analyzed. The results indicate that the superior activity is mainly ascribable to the incorporated Cu diatomic site, which not only enhances the spectral response ability but also accelerates the transfer and separation of photoexcited charge carriers of tri-3s-triazine framework. The present study provides a fascinating inspiration to synthesis a binuclear-site catalysts for highly selective CO_2 reduction.

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(P-68)

Excimer Formation in Polycrystalline PBI Films: Dependence on Packing Geometry

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I am Seongsoo Kang, and I have earned a Ph.D. degree in the field of photophysical chemistry utilizing laser spectroscopy at Yonsei University. My primary focus during my studies was conducting photophysical analyses of various organic and inorganic systems.

This study investigates how packing geometries influence excited-state dynamics in films of perylene bisimides (PBIs). The molecular structure of PBIs was modified to control how they are packed in the solid state, and PBI films were fabricated on SiO2 substrates using physically evaporated deposition method.[1] Three films of each PBI exhibited distinct steady-state absorption and emission spectra. Excimer-like states were observed in **PBI1** and **PBI2**, with the degree of excimer formation dependent on the orientation and packing of **PBI** molecules within the film. Interestingly, **PBI2** showed minimal changes in absorption spectra, except for a slight redshift and spectral broadening, compared to the monomer's steady-state absorption spectra.[2] Femtosecond transient absorption spectroscopy measurements confirmed this peculiarity. We suggest that thermal motion and intermolecular interactions can overcome the steric hindrance of PBI2 molecules, causing structural changes in the excited-state. This study provides a better understanding of how crystalline order impacts excited-state dynamics and the formation of the excimer-like state.

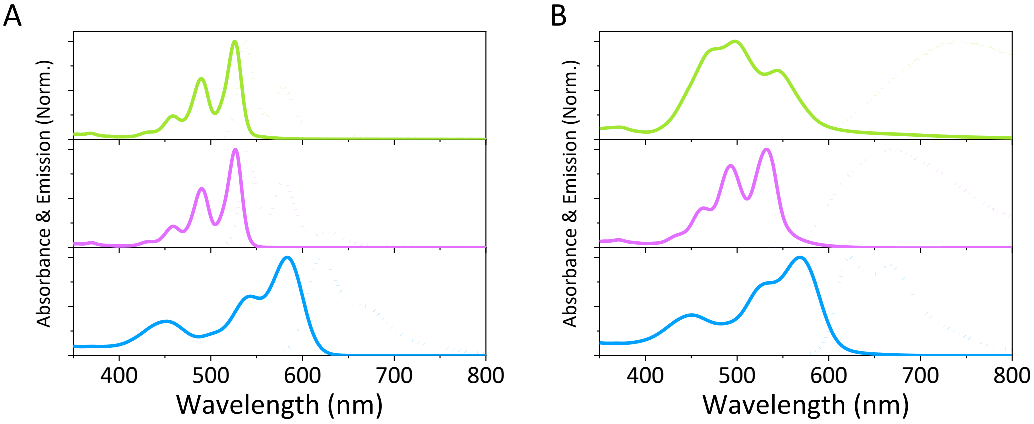

Figure 1. Steady-state absorption and emission spectra in (A) monomeric PBIs in dichloromethane (B) polycrystalline PBI films (upper: **PBI1**, middle: **PBI2**, and bottom: **PBI3**)

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(P-69)

Energy Prediction of HF-DFT in Ice Structures

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HF-DFT, a practical version of density-corrected density functional theory(DC-DFT), has demonstrated significant advances in a variety of chemical reactions.[1] In addition, by incorporating Grimme's dispersion correction term in a more elaborate manner, the newly developed HF-r^2SCAN-DC4 functional exhibits remarkable performance within cluster systems, including pure water and noncovalent interactions which is vital in biomolecules.[2] In this study, the application of the functional was further extended by benchmarking periodic ice structures. Since energy prediction of the ice structures leads to accurate prediction of the phase diagram of ice water, the benchmark set is considered important and many studies are being conducted. By comparing the absolute and relative cohesive energies of the ice structures with reference values[3] and other relevant works, the reliability and accuracy of the HF-r^2SCAN-DC4 functional were evaluated. The results not only highlighted the performance of the HF-r^2SCAN-DC4 functional but also provided further validation of its potential as a versatile tool for modeling a wide range of biochemical systems.

References

(P-70)

Ultrafast Aromatization Process in 1,6-methano[10]annulene

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Baird's rule of reversed aromaticity in the T_1 state and its extension to the excited singlet (S_1) state have been verified only by theoretical and computational methods until recently. We suggested effective experimental spectroscopic tools that provide direct evidence of the excited state aromaticity. In particular, the vibrational analysis critically supported the aromaticity reversal in the S_1 state instead of quantum calculations due to computational difficulties in the excited singlet (Sn) state. Tovar, Casado, and co-workers reported the synthesis of TMTQ molecule,[1] which is a 1,6-methano[10]annulene (M10A) co-oligomer with thiophene and dicyanomethylene units on both sides of core M10A moiety. A significantly small ΔE_{ST} gap was observed in TMTQ and the T_1 state stabilization by Baird's rule was proposed to account for this phenomenon. According to this perspective, we have demonstrated the aromatization of TMTQ in the excited state induced by an intramolecular CT process via electronic and vibrational spectroscopic analysis.[2] In this work, ultrafast aromatization process accompanied with the structural rearrangement along M10A ring were investigated by using 10 fs pulse. Broad-band transient absorption spectroscopy along with NAMD simulation by MRSF method were carried out to explore the ultrafast aromatization process accompanied with bond length alternation to prepare the structural planarization of nonaromatic M10A unit.

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(P-71)

Photoelectrochemical CO_2 Reduction Using an Efficient Bismuth doped-TiO_2 Photoanode and Cu_2O-dark Cathode

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Many earth-abundant n-type oxide semiconductors operate efficiently in solar light photocatalysis, such as TiO_2, WO_3, $BiVO_4$, Fe_2O_3, etc. Metallic and composite electrocatalysts can be employed as cathodes, depending on n-type semiconductors serving as photoanodes. Using these devices, CO_2 is reduced with high faradic efficiency, specifically to highly reduced products such as CH_4 and C_2H_4. Essentially, it is a PEC cell that uses photoanodes to reduce CO_2. In n-type semiconductors, TiO_2 is abundant, nontoxic, cost-effective, stable, and has a suitable bandgap energy (3.2 eV) for CO_2 reduction. The main drawback is the poor photogenerated charge carriers, as well as the rapid surface and bulk charge recombination that results from the rapid oxidation of water.

In this thesis, an effective electron transfer to the dark cathode can be achieved by incorporating a single atom of Bi into the TiO_2 lattice as a photoanode material in PEC water oxidation reaction. The selectivity of by-products in this PEC CO_2 reduction was investigated by using Pt-metal or Cu-based dark cathodes. A fourfold increase in photocurrent density was observed for water oxidation using Bi-TNR compared to bare TNR. The photoanode was maintained for a long period (20 h) to demonstrate the stability of the photoanode. For the CO_2 reduction reaction, Pt-metal and Cu-based dark cathodes were compared using Bi-TNR as a photocathode. This result has enhanced the FE and selectivity of a Cu-based dark cathode assembled with Bi-TNR. Using nonprecious metals dispersed at atomic scales as co-catalysts for sustainable solar energy-driven energy conversion and storage, this study opens a new window for good utilization of non-precious metals.

Keywords: Titanium dioxide, Bismuth, Copper oxide, Photoelectrochemical cell, CO_2 reduction.

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(P-72)

The Dynamics of Bimolecular Proton Transfer in Aqueous Solution Using Time-resolved Vibrational Spectroscopy

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The neutralization of an acid by a base is one of the fundamental reactions that occur in solution. In previous studies, acid-base reactions involving excited photoacid have typically been investigated at high base concentrations, [1, 2] but the mechanisms at lower base concentrations remain to be clarified. We observed the kinetics of acid-base reactions induced by the excited photoacid, pyranine (DA), in the presence of azide ions (N3−) in D2O solution using by femtosecond vibrational spectroscopy. Specifcally, the spectral characteristics of four species (DA, electronically excited DA (DA*), the conjugate base of DA* (A*−), and the conjugate base of DA (A−)) were probed in the spectral region of 1400–1670 cm−1 in the time range of 1 ps–1 µs. This broad time range covers all acid-base reactions initiated by photoexcitation at 400 nm, allowing us to investigate both DA* and A- related reactions. In addition, population changes of N3− and DN3 were monitored using absorption bands at 2042 and 2133 cm-1, respectively. After excitation, about half of DA* relaxed to DA with a time constant of 0.44±0.04 ns. The remainder underwent an acid-base reaction to produce A*−, which relaxed to A− with time constant of 3.9±0.3 ns. The acid-base reaction proceeded via two pathways: exchange with the added base or simple deuterium release to D2O (protolysis). Notably, all acid-base reactions were well described by the steady-state limit. Thus, the acid-base reactions at low base concentrations (<0.1 M) were diffusion controlled, they could be described using a simple rate equation.

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(P-73)

Combining Hole Selective and Electron Transport Interfaces to Improve $CuFe_2O_4$ Thin-Film Photoelectrochemical Water Splitting

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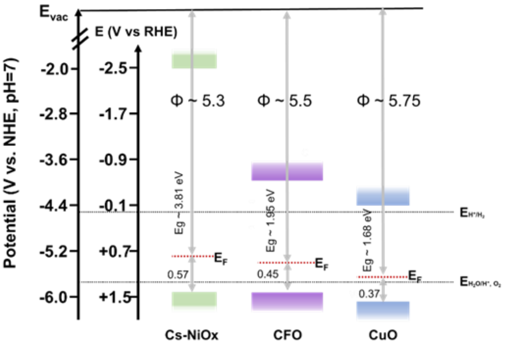
In cost-effective photoelectrochemical (PEC) water-splitting cells, ternary oxide photoelectrodes, particularly copper ferrite photoelectrodes, have demonstrated promising performance. A number of inherent challenges have prevented the photocurrent density of bare $CuFe_2O_4$ (CFO) from meeting theoretical expectations, including a high rate of photogenerated charge carrier recombination, slow surface hydrogen evolution reaction kinetics (HER), and limited charge transport across the substrate interface. In this study, we introduce a Hole-Selective Layer (HSL) under the CFO layer to facilitate photogenerated hole selectivity, and a thin-CuO outer layer to enhance HER kinetics at the surface. A Hole-Selective Layer has been demonstrated to be crucial in improving photogenerated hole conductivity and interface charge transfer. In addition, various analytical methods have been employed to examine the significant contributions of the CuO outer layer to the CFO photocathode for surface water reduction kinetics. As a result, the optimal HSL/CFO/CuO photoelectrode exhibited a remarkable photocurrent density of -0.81 $mA\cdot cm^{-2}$ at 0.4 VRHE. This accomplished photoelectrochemical performance is ≈7.4-fold times higher than that of the bare CFO. Furthermore, the photon-to-electron conversion efficiency (IPCE%) increased over the solar spectrum when compared to bare CFO, and it reached ≈30% at 400 nm. Overall, the results demonstrate that the proposed fabrication method represents a considerable advance in the development of affordable water-splitting cells.



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(P-74)

Elucidating Charge-Carrier Dynamics of Photocatalysts with Femtosecond Time-resolved X-ray Absorption Spectroscopy via XFEL

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Transition metal oxide is a promising candidate for solar energy conversion and photocatalysts due to its unique properties. However, the influence of surface structures on its dynamic changes remains unclear. In this study, we employed femtosecond X-ray absorption spectroscopy to explore the electron dynamics between TiO_2 and surface-engineered blue TiO_2, aiming to gain insights into their electronic and structural changes, as well as charge transfer dynamics. Through static analysis, we observed distinct differences in the pre-edge region, indicating significant alterations in the structure and electronic properties. Specifically, we found that the presence of oxygen vacancies in blue TiO_2 led to a noticeable increase in the A2 peak at the pre-edge region, suggesting a distorted structure. Utilizing time-resolved experiments, we further identified a positive feature in the pre-edge region and two positive peaks in the edge region. Interestingly, both TiO_2 and blue TiO_2 exhibited similar rising and decay components in the pre-edge region, while in the edge region, TiO_2 displayed two components, whereas blue TiO_2 showed only one. Despite the limited impact of surface oxygen vacancies on the rate of electrical and structural changes, they induced notable differences in the charge transfer mechanism between the two samples. By employing time-resolved X-ray absorption spectroscopy (TRXAS), we directly investigated the electron dynamics of TiO_2 and blue TiO_2, anticipating that the dynamic information obtained can provide valuable insights for the design of catalyst systems.

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(P-75)

Fifth-Order Multidimensional Spectroscopy for Ground-State Chemical Reactions: Simulation using Equation-of-Motion Phase-Matching Approach

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We are currently developing innovative fifth-order multidimensional spectroscopy techniques, namely two-dimensional Raman-infrared (2DRIS) and two-dimensional Raman-electronic (2DRES) spectroscopies, to effectively investigate the reactive modes of ground-state chemical reactions. While spectroscopic methods for studying excited-state reactions have advanced significantly, typical techniques for ground-state reactions have limitations. Therefore, our goal is to overcome these limitations and provide valuable insights into ground-state dynamics.

In this study, we present a theoretical description of the two fifth-order multidimensional spectroscopy techniques, employing the equation-of-motion phase-matching-approach (EOM-PMA) method. This method offers an effective and cost-efficient approach for calculating N-wave mixing signals within the desired time scale. By simulating the 2DRIS and 2DRES signals for a model system using the EOM-PMA, we demonstrate that the fifth-order signals can be distinguished from lower-order signals. Additionally, we propose a data analysis method for both techniques.

The simulation results indicate that our proposed spectroscopic approaches hold promise for experimental realization. By successfully separating the fifth-order signals, we provide a foundation for the future application of 2DRIS and 2DRES. We believe that this simulation study will be instrumental in advancing these multidimensional spectroscopy techniques and facilitating their practical implementation.

In conclusion, our work focuses on the development and theoretical investigation of new fifth-order multidimensional spectroscopy techniques: 2DRIS and 2DRES. By simulating the signals and proposing data analysis methods, we demonstrate the potential of these techniques for studying ground-state chemical reactions. We hope that our efforts will contribute to the experimental realization and widespread adoption of 2DRIS and 2DRES, enabling further understanding of ground-state dynamics in chemical reactions.

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(P-76)

Tracking the Photo-Induced Relaxation Mechanism of 2-Thiouracil via Time-resolved X-ray Absorption Spectroscopy

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Uracil is the one of nucleobases in the RNA, which has inherent photo-protective mechanism to prevent from harmful UV radiation. In specifically, when UV light is radiated to uracil, the excited state relaxation occurs very fast along the singlet pathways. However, thionation of exocyclic oxygen to sulfur can change this inherent biochemical feature to a new one. This noncanonical nucleobase has large spin-orbit coupling between the excited singlet and triplet states, so intersystem crossing happens more dominantly in 2-thiouracil than uracil. The excited triplet states decay to ground state slowly and have high reactivity so that it could be used to biotherapeutic ways. In this regard, we report time-resolved X-ray absorption spectroscopy results to study excited state dynamics of 2-thiouracil and plan to analyze UV excitation decay dynamics. $S_1(n\pi^*)$ state is optically blind dark state so that transient absorption spectroscopy cannot see the forbidden S_1 state. But the X-ray probes, especially S K-edge can directly probe elemental specific electronic structure near S atom environment. So, we expect to trace the non-adiabatic internal conversion from $S_2(\pi\pi^*)$ to S_1 at the conical intersection of two potential energy surface, or intersystem crossing to triplet $\pi\pi^*$ or $n\pi^*$ states. The energy dependent time trace results show that a fast dozens of femtoseconds scale component indicates the non-adiabatic internal conversion through the conical intersection between S_2 and S_1. The sequential kinetic model analysis can explain the experimental time dependent X-ray absorption spectra.

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(P-77)

Computer-Aided Design of Visfatin-Derived Small Peptides with Angiogenic Activity

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Angiogenesis plays an important role in female reproduction including development of follicles and implantation. Visfatin which is secreted from various tissues not only enhances the expression of vascular endothelial growth factor (VEGF), but also exhibits angiogenic effect itself. In this study, we designed visfatin-derived small peptides which mimic angiogenic activity of visfatin by using computer-aided drug design (CADD) techniques. Firstly, peptide library was derived using peptide overlapping method with active site of visfatin. Molecular docking simulation is implemented to estimate the binding affinity of designed peptides. Finally, molecular dynamics (MD) simulation is implemented to investigate the structural stability of visfatin-peptide complexes.

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(P-78)

Investigating the Photochemical Behavior and Identifying Linkage Isomers of S-Nitroso-Mercaptoethanol at Room Temperature

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Nitric oxide (NO) is a vital signaling molecule involved in regulating various physiological and pathological pathways.[1] S-Nitrosothiol (RSNO), produced by nitrosylation of thiols, plays a crucial role in transmitting and regulating NO signals in biological systems. RSNO serves as a carrier of short-lived NO radicals and has been extensively used as a tracer and experimental donor for investigating NO-dependent signaling mechanisms. Photoactivation kinetics of RSNO is of significant interest for developing RSNO-based therapeutics and understanding photoactive NO mechanisms in biological systems.[2]

Nitrosyl compounds, including nitrosyl metal complexes and RSNO, exhibit linkage isomers with different lifetimes.[3] The presence of linkage isomers can affect the efficiency of NO delivery drugs and induce unwanted reactions. In the liquid phase, excited RSNO populations may not always dissociate, leading to the formation of isomers not observed in the gas phase. Previous studies have analyzed the photodissociation kinetics of water-soluble RSNOs and identified intermediates, indicating the involvement of electronic transitions.[4] S-nitroso-mercaptoethanol (MceSNO), a simple structured water-soluble RSNO, was used to measure the temperature-dependent rate constant of its linkage isomer. The electronic absorption spectrum of MceSNO in D_2O revealed distinct transitions, and the equilibrium IR spectrum confirmed the presence of a NO stretching peak. Time-resolved IR spectroscopy was employed to study the linkage isomer of MceSNO at room temperature. Understanding the characteristics and behavior of RSNO and its isomers has important implications for the development of RSNO-based therapeutics and the investigation of photoactive NO mechanisms in biological systems.

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(P-79)

Study of poly(alkylene carbonate) based solid polymer electrolytes using FTIR and 2DIR spectroscopies

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In the last few decades, polyethylene oxide (PEO) based solid polymer electrolytes (SPEs) have been attracted because of high solvation power of PEO, good mechanical properties, and improved safety towards to conventional liquid electrolytes. However, low ionic conductivities of conventional PEO based SPEs are one of major problem of SPEs. Moreover, narrow electrochemical window of PEO also limits further applications of PEO based SPEs. To overcome these drawbacks, many researchers have tried to make SPEs with other polymers and several polymers including polycarbonates show higher performances than PEO[1, 2]. Among those polymers, we focused on polyethylene carbonate (PEC) and polypropylene carbonate (PPC) because they have carbonyl groups which are sensitive to changes of surroundings. In this study, we investigated PEC and PPC based SPEs with FTIR and 2DIR spectroscopies and acquired structural and dynamics information about those SPEs.

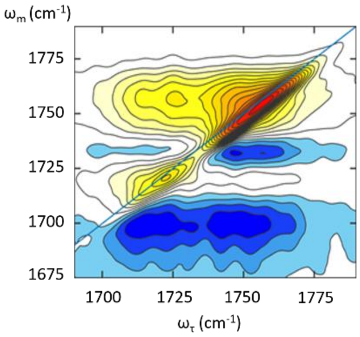

Figure 2. 2DIR spectra of PEC/LiClO4 film at 30ps. Cross peaks at the upper-left and lower-right are growing as the waiting time increases.

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(P-80)

Light-driven electron dynamics of the photoactive yellow protein derivatives: Role of the S1 intermediate state

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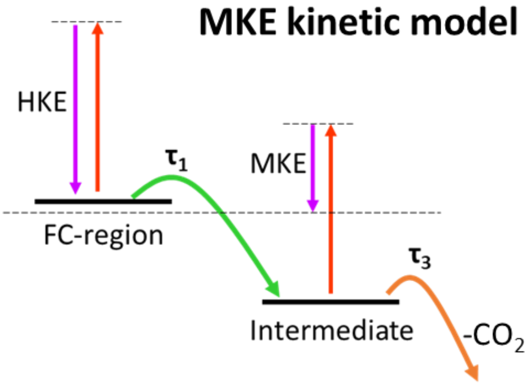
Herein, we investigated the real-time dynamics of the first singlet electronic excited state (S_1) of deprotonated para-coumaric acid (pCA$^-$) and deprotonated para-coumaric ester (pCE$^-$) using nanosecond spectroscopy and femtosecond time-resolved spectroscopy combined with a cryogenically-cooled Paul ion trap. By measuring the S_1 lifetimes, we observed distinct relaxation dynamics for each derivative. In the case of pCE$^-$, the initial S_1 state bifurcates into a twisted intermediate and undergoes an internal conversion (IC) process leading to the Dipole-Bound state (DBS). Both of these bifurcated states subsequently undergo autodetachment, resulting in the loss of an electron from the chromophore. Interestingly, in pCA$^-$, the initial S_1 state relaxes into an intermediate state characterized by a remarkably long lifetime. This intermediate state undergoes IC directly to the ground state (S_0), inhibiting autodetachment. We obtained evidence for this IC process by observing CO_2 fragmentation, indicating the generation of a hot S_0 state. The kinetic competition between autodetachment and IC in the intermediate state was thoroughly investigated through fragment action spectroscopy and time-resolved experiments. These findings provide valuable insights into the photoisomerization of the photoactive yellow protein.



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(P-81)

Temperature-dependent effect of the solvent cage on I_3^- in the deeply supercooled solution

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Solvent-solute interaction is one of the key factors to comprehend various mechanisms and properties of the molecules. One such interaction is the hydrogen bonding interaction, which is common in aqueous solutions. Recent studies on I_3^- revealed that the hydrogen-bonding solvents make the solute have an asymmetric and bent structure due to the strong solvent-solute interaction. Since it is well known that the hydrogen bonding network gets stronger at supercooled temperatures, we have studied I_3^- in supercooled solution to understand the effect of the enhanced solvent-solute interaction (Figure 1).

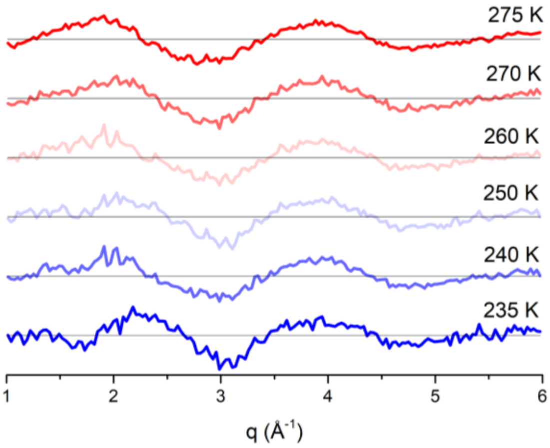

Figure 3 Temperature-dependent isotropic patterns from deeply supercooled solution droplets 1 ps after the laser excitation; 275 K (top) to 235 K (bottom)

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(P-82)

Transformation of bimetallic NiCo-oxide into trimetallic PtNiCo-alloy via pulsed laser technique for enhanced hydrogen evolution reaction

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The development of highly efficient and low-cost electrocatalysts for the hydrogen evolution reaction (HER) is of utmost importance in assembling clean and sustainable energy systems. Trimetallic alloys, with their unique properties such as synergistic effects and tunable electronic structure, have emerged as promising candidates for catalyzing the HER. In this work, we report a new approach for transforming bimetallic NiCo-oxides into trimetallic PtNiCo-alloys using a pulsed laser technique. The resulting PtNiCo-alloys were then used as electrocatalysts for the HER. Numerous characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), Raman spectroscopy, X-ray photospectroscopy (XPS) were utilized to analyze and characterize the synthesized electrocatalysts. Furthermore, the electrocatalytic performance of the synthesized PtNiCo-alloys for the HER was examined in a 1 M KOH electrolyte. The obtained results demonstrate that the optimized PtNiCo-alloys exhibited an outstanding HER performance with a low overpotential of 73 mV at 10 mA cm^{-2}. This performance is comparable to that of the benchmark Pt/C catalyst. Therefore, this work presents a new and rapid synthetic strategy for developing effective electrocatalysts to enable efficient hydrogen production.

About Author: Mr. Akash is currently pursuing a Ph.D. degree at Department of Chemistry, Gyeongsang National University, South Korea, under the guidance of Prof. Myong Yong Choi. He received master's degree in Nanotechnology from Periyar Maniammai Institute of Science and Technology, Tamil Nadu, India in 2020. His current research is focused on the development of electro and photocatalysts for energy and environmental remediation, mainly, wastewater treatment and clean hydrogen production

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(P-83)

High-entropy alloys on MWCNT with Ir, Au, Pd, Pt and Ru with PLI for hydrazine electrolysis performance via in-situ Raman spectroscopy

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High Entropy Alloy (HEA) is a new type of single-phase solid solution material with more than 5 metals. High entropy alloys have potentials due to their excellent properties such as thermal stability at high temperatures, and excellent destructive personality at very low temperatures. In this research, we synthesized successfully high-entropy alloy (HEA) nanoparticles on surface of carbon nanotubes (CNT) via pulsed laser irradiation. The synthesized samples' characterizations were investigated from TEM, XRD, XPS, ICP and so on. Our HEA (Ir, Au, Pd, Pt, and Ru)/CNT samples were confirmed the single-phase fcc structures from XRD results. Also, their TEM images show HEA with ca. 2 nm size were well-defined on CNT surface. In addition, the electrochemical test was performed not only at HER and OER, but also at hydrazine oxidation reactions, and excellent efficiency was observed. In additional, the real-time monitoring of H_3O^+ during HER via in situ electrochemical Raman spectroscopy revealed an acidic environment.

About Author: Ms. Chae Eun Park is a Masters graduate student at the Department of Chemistry, Gyeongsang National University (GNU). Her major research is focused on development of various nanoparticles and hybrid nanomaterials by using pulsed laser technique. She has also studied the performance of electrocatalyst for photoelectrochemical reactions, direct hydrogen fuel cells, HER, OER, and overall water splitting etc.

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(P-84)

A broad class of semi-local DFT ingredients from fractional calculus

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The current development of DFT is focused on discovering the exact density functional, which is known to be non-local [1]. However, most current density functional approximations (DFAs) rely on only local ingredients such as $\boldsymbol{\rho}$, its gradient, and local kinetic energy, which limits DFAs' non-locality. Recently developed functionals incorporate non-local local Hartree-Fock energy [2, 3], but this feature requires large computation time or specific approximations [3, 4, 5]. The usage of other non-local features [6, 7, 8] in machine-learned functionals also has similar problems. To address this issue, we adapted fractional calculus to create a new class of non-local ingredients, $\boldsymbol{\xi^{\alpha}}$ $(\boldsymbol{\alpha} \in (\infty, \mathbf{1}]))$. These ingredients can be computed at a cost similar to that of the local kinetic energy and provide complementary information to traditional DFT ingredients. By using $\boldsymbol{\xi^{\alpha}}$'s to train neural networks, we achieved highly accurate predictions for the exact exchange. Our findings suggest that the incorporation of novel features can improve the accuracy of functionals, leveraging the power of machine learning techniques.

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(P-85)

Pulsed laser synthesis of Pd/PdO decorated nickel phosphate as an efficient bifunctional catalyst for electrochemical overall Hydrazine splitting

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Water electrolysis is the most promising environment-friendly approach for generating hydrogen on a large scale with the highest efficiency and purity. It is governed by hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) processes, but the sluggish OER is more decisive and rate-determining. The hydrazine oxidation reaction (HzOR), as a substitute for the sluggish OER, is identified as a promising strategy for hydrogen production through water splitting. The most recent hydrogen evolving electrocatalysts with the highest performance are noble metal-based catalysts (i.e., Pt, Rh, Ru and Ir). However, these metals are finite in the earth crust, which limits their wide application. Therefore, extensively studied transition metal-based electrocatalysts which could be the alternatives to an expensive noble metals. Metal phosphate, as a new series of electrocatalysts, have been attracted enormous attentions owing to its unique lattice structure geometry. The phosphate group not only benefits for the adsorption of water molecule but also facilitates the oxyhydrate of metal site and dissociation of water. In this work, we produce $Ni_3(PO_4)_2.8H_2O$ electrocatalysts via pulsed laser irradiation in liquid (PLIL) and explored the phase-selective active-sites in electrocatalytic HER and HzOR, respectively. Further, Pd nanoparticles were incorporated by PLIL process to enhance the active sites of $Ni_3(PO_4)_2.8H_2O$ catalysts. The synthesized catalysts were characterized using various analytical techniques such as XRD, FE-SEM, EDS, Raman, and FT-IR. This work shows PLIL-synthesized electrocatalysts as a promising candidates for hydrazine-assisted electrolytic hydrogen production.

About Author: Ms. Hyeyeon Lee is pursuing a master's degree at Gyeongsang National University, and intends to synthesize nanomaterials using laser techniques and apply as electrochemical catalysts.

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(P-86)

Real-time Study of Methylene Blue Aggregation under aqueous and organic solvent via Acoustic Levitator: A Spectroscopic and DFT study

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The acoustic levitation is a novel and unique technique enables container-less processing of single levitated droplets. This can avoid complex effects that occur at the contact surfaces of materials, such as reaction vessels, and increase the sensitivity of spectral detection techniques such as Raman spectroscopy, Ultraviolet-Visible (UV-Vis) spectroscopy, Fourier-transform infrared spectroscopy, and Intensified charge-coupled device (ICCD) camera. Herein, we studied the dimerization of methylene blue using various solvents (organic and aqueous) via acoustic levitator. The dimerization of methylene blue is greatly affected by the dielectric constant of the solvent medium. We observed real-time reactions by altering the composition of solvents, which directly influence the dimerization of methylene blue. Besides water droplet, the UV-visible spectrum shows the changes in the resolved two peaks when methanol and ethanol was used as solvent. Interestingly, we could observe the dimerization phenomenon in methanol and ethanol solvents due to the evaporation of droplet, which could be difficult to observe in the container reaction due to its low dielectric constant compared to water medium. Moreover, acidic protonation shows a change in the direction of aggregation of the MB molecules. These results were further confirmed through DFT calculations.

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(P-87)

Mechanistic studies of the conversion of bimetallic NiCo-oxide into NiCo-alloy via a novel pulsed laser irradiation technique

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In this study, we investigate the conversion mechanism of NiO, Co_3O_4 and $NiCo_2O_4$ to their respective Ni, Co and NiCo-alloy via one-pot pulsed laser irradiation in ethanol without utilizing a reducing agent. The conversion mechanism was comprehensively studied through the utilization of X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet-visible (UV-vis) spectroscopy and Fourier-transform infrared (FT-IR) spectroscopy techniques. The continuous pulsed laser irradiation effectively melted and merged the agglomerated particles into a single large particle. Specifically, the characterization results confirmed the successful reduction of NiO, Co_3O_4, and $NiCo_2O_4$ to their respective metals (Ni, Co, and NiCo-alloy) through the involvement of ethanol decomposition products. This finding highlights the significant role of ethanol decomposition products as reducing agents in the conversion of oxides to metals. Our study provides a plausible mechanism for understanding the pulsed laser reduction of metal oxides into metal nanoparticles.

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(P-88)

Rational synthesis of Ir doped NiFe-LDH nanosheets by pulsed laser strategy for boosting oxygen evolution kinetics

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Water electrolysis is one of the prominent and clean technologies that generate hydrogen energy by splitting water molecules. However, the hydrogen production efficiency in water electrolysis was largely affected from the sluggish reaction kinetics of anodic oxygen evolution reaction (OER). Thus, it is still important to design more suitable electrocatalysts for the OER. In this study, we synthesized iridium-doped NiFe-layered double hydroxides (NiFeIr-LDH) nanosheets using the pulsed laser irradiation (PLI) method. The electrocatalytic activity of NiFeIr LDH nanosheets was explored for the OER using a 1 M KOH electrolyte. The achieved results reveal that NiFeIr-LDH nanosheets showed a low overpotential (246 mV @ 10 $mA \cdot cm^{-2}$) and small Tafel slope (52 $mV \cdot dec^{-1}$), indicating its outstanding OER performance. In addition, it is confirmed through the in-situ/operando Raman spectroscopy that the surface formed intermediates such as γ-NiOOH and Ir-O plays an important role in improving OER performance of NiFeIr-LDH. As a result, the two-electrode alkaline water electrolyzer with NiFeIr-LDH(+)‖Pt/C(-) needed a cell voltage of only 1.53 V @ 10 $mA \cdot cm^{-2}$, which is lower than IrO_2(+)‖Pt/C(-) electrolyzer (1.62 V @ 10 $mA \cdot cm^{-2}$). This work provides a new method of developing an efficient and stable OER electrocatalysts for alkaline water electrolysis.

About Author: Mr. Sieon Jung is currently pursuing a master's degree at Gyeongsang National University, South Korea, under the guidance of Prof. Myong Yong Choi. His current research focuses on synthesizing nanomaterials using pulsed laser techniques. His is currently conducting research to synthesize electrocatalysts using pulsed laser techniques for various energy-related applications such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), hydrogen oxidation reaction (HzOR), and methanol oxidation reaction (MOR).

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(P-89)

Anion-modulated Cobalt Composites with Remarkable Electrocatalytic Performance: In Situ/Operando Raman Studies

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Herein, we produced cobalt phosphate ($Co_3(PO_4)_2$), cobalt oxide (Co_3O_4), and cobalt sulfide (Co_9S_8) electrocatalysts via pulsed laser ablation in liquids (PLAL) technique to explore the synergy of anion modulation in electrocatalytic HER and OER [1, 2]. The $Co_3(PO_4)_2$ affords an ultralow overpotential of 230 mV at 10 mA cm^{-2} with a 48.5 mV dec^{-1} Tafel slope which outperforms the state-of-the-art Ir/C in OER owing to its high intrinsic activity. Whereas, the Co_9S_8 exhibits the highest HER performance among synthesized Co-based catalysts with the lowest overpotential of 361 mV at 10 mA cm^{-2} with a small Tafel slope of 95.8 mV dec^{-1} in an alkaline medium and produces H_2 gas with ~500 mmol g^{-1} h^{-1} yield rate under the fixed -0.45 V vs. RHE potential. Thus, the identified surface reactive intermediates over in-situ EC-Raman spectroscopy revealed that cobalt (hydr)oxides with higher oxidation states of Co cation forming under oxidizing potentials on the electrode-electrolyte surface of $Co_3(PO_4)_2$ facilitate the OER, and $Co(OH)_2$ drives the HER. Notably, the fabricated two-electrode water electrolyzers using $Co_3(PO_4)_2$, Co_3O_4, and Co_9S_8 electrocatalysts can deliver the cell potential of 2.01 V, 2.11 V, and 1.89 V, respectively, at current densities of 10 mA cm^{-2} [3]. This work shows PLAL-synthesized electrocatalysts as promising candidates for water splitting and provides an underlying principle for advanced energy conversion catalysts and beyond.

The presenting author, Talshyn Begildayeva, is currently a Ph.D. candidate under the guidance of Professor Myong Yong Choi in the Department of Chemistry at Gyeongsang National University. Areas of interest include material synthesis via laser-assisted methods (i.e., pulsed laser ablation (PLAL) and irradiation in liquids (PLIL)), material characterization, and further assessment in energy conversion applications.

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(P-90)

High valence Mo doped Ni/NiO nanocomposite: an efficient electrocatalyst for the energy-saving hydrogen production via enhancing urea oxidation kinetics

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Electrocatalytic urea oxidation reaction (UOR) has attracted much interest to replace anodic oxygen evolution reaction in water electrolysis because of its favorable thermodynamic overpotential. However, UOR remains hindered from its slow reaction kinetics, high energy barrier, and complex mechanism. Thus, developing high-efficiency electrocatalysts for the UOR is most essential. Herein, we propose a rapid and novel method for synthesizing Mo-doped Ni/NiO (Ni/MNO) nanocomposite, and it is used as a highly effective electrocatalyst for the UOR. It is interesting to note that when high-valence Mo doped into the Ni/NiO nanocomposite, the Ni atoms can facilitate the oxidation of Ni^{2+} into Ni^{3+} and offer a huge number of active sites during the electrochemical process, which could be improve UOR performance. As expected, the Ni/MNO catalyst showed a remarkable electrochemical performance for the OER and UOR than that of pure Ni/NiO catalyst. This improvement could be mainly ascribed to the significant doping impact of Mo, effective structural modulation, enhanced active sites, and availability of more Ni^{3+} cations. The optimized Ni/MNO-10 catalyst exhibited a low overpotential of 280 mV for OER and a low working potential of 1.37 V *vs.* RHE for UOR at 10 mA cm^{-2} with amazing catalytic durability over 12 h. In addition, the fabricated Ni/MNO-10(+)‖Pt/C(-) electrolyzer needed a lower cell voltage of 1.45 V to supply 10 mA cm^{-2} in urea-assisted water splitting (UWS) than that of its overall water splitting (OWS) of 1.65 V at 10 mA cm^{-2}. As well, it possessed an outstanding durability over 12 h at 10 mA cm^{-2}. This work offers a rapid and effective approach to designing low-cost and highly efficient electrocatalysts for both clean energy production and wastewater treatment.

About Author: Velusamy Maheskumar received his M. Sc and PhD degrees from the Department of Physics, Karunya Institute of Science and Technology in 2014 and 2018, respectively. He is currently a Postdoctoral researcher in Laser Photochemistry Laboratory, Gyeongsang National University. His research interest is centered on the design and preparation of nanomaterials and their application of photo and electrocatalysis.

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(P-91)

Synthesis of $Co(OH)_2$/rGO electrocatalysts using a dual laser system for oxygen evolution kinetics

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Pulsed laser-assisted synthesis strategy is currently recognized as an environmentally friendly and efficient method for the development of electrocatalytic nanomaterials. In this study, $Co(OH)_2$ incorporated reduced graphene oxide (rGO) nanosheets were produced using a single-step pulsed laser irradiation process. Initially, graphene oxide was reduced to rGO using ascorbic acid as a mild reducing agent through pulsed laser irradiation. Subsequently, the synthesized rGO and $Co(OH)_2$/rGO materials were systematically characterized using various analytical techniques, including X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The electrochemical properties of $Co(OH)_2$/rGO in the oxygen evolution reaction (OER) under alkaline conditions were investigated, and the effect of $Co(OH)_2$ loading on the efficiency of oxygen evolution was examined. Additionally, the role and mechanism of $Co(OH)_2$ in the OER reaction were confirmed through in situ Raman spectroscopy. The obtained results indicate that $Co(OH)_2$/rGO nanocatalysts hold promise as materials for electrochemical energy production applications.

About Author: Ms. Yeryeong Lee is currently pursuing her Masters course from GNU. Her Masters research includes synthesize electrocatalytic nanomaterials using pulsed laser technique for HER, OER, and overall water splitting applications

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(P-92)

Facile One-pot Synthesis of Nickel Sulfoselenide via Pulsed Laser Ablation for Oxygen Evolution Reaction

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Modulating the active site is one promising strategy to increase catalytic performance. Herein, we could successfully introduce anion substitution to transition metal chalcogenides (TMCs) via pulsed laser ablation (PLA) technique. Nickel sulfoselenide ($Ni_3Se_{4(1-x)}S_{4x}$), nickel selenide (Ni_3Se_4), nickel sulfide (NiS/Ni_3S_4) were prepared by one-pot facile PLA method for anodic reaction in water electrolysis system. The synthesized materials were characterized by XRD, Raman, FE-SEM, HR-TEM, and XPS analytical techniques. The activity of these catalysts was evaluated by examining the electrochemical oxygen evolution reaction (OER). Nickel sulfoselenide revealed best activity with low overpotential of 327.4 mV at a constant current density of 10 mA cm^{-2} which indicate the proliferation of active sites. While nickel selenide and nickel sulfide showed overpotential of 348.4 mV and 361 mV, respectively. This work demonstrates facile and advanced strategy in the preparation of sulfur modified TMCs electrocatalysts toward high-performance for OER.

About author: Ms. Yewon Oh is a Masters graduate student at the Department of Chemistry, Gyeongsang National University (GNU). Her major research is focused on preparation of electrocatalysts and nanomaterials through pulsed laser ablation and irradiation techniques in liquid medium. She has also studied the performance of electrocatalyst for detection of heavy metals and electrocatalytic reactions like HER, OER, and overall water splitting applications.

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(P-93)

Stomach tissue classification using autofluorescence and machine learning

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Autofluorescence is a non-invasive analysis method which is used to diagnosing for in vivo and ex vivo tissues. Normally, Autofluorescence appears at a wavelength of 400 nm to 700nm and includes various biometric information. Among them Nicotinamide dinucleotide (NADH) and Flavin adenine dinucleotide (FAD) are co-enzymes used in metabolism and respirations, which are strongly associated with pathological symptoms. Changes in metabolism and composition of substances lead to subtle variations in the fluorescent spectrum, which exhibit different tendencies depending on the characteristics of the tissue. In this study, we conducted research on classifying the mucosa, submucosa, and muscle of the stomach tissue using a combination of hyperspectral imaging for fluorescent measurements and machine learning models. Hyperspectral imaging, as a multi-channel imaging technique incorporating spatial and spectral information, enables detailed analysis of tissue characteristics at a fine level. In order to perform semantic segmentation of hyperspectral images, we employed an ensemble approach using the bagging tree method in machine learning to classify the pixels. This allowed us to conduct classification and visualization tasks for gastrointestinal tissue.

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(P-94)

Extension of long-range corrected density functional theory including a two-Gaussian Hartree-Fock operator to core-excitation energy calculations of third row atoms

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Previously, we presented an improved long-range corrected (LC) density functional theory (DFT), named LCgau-core-DFT [1,2], for high accuracy calculations of the core excitation calculations of the 2nd-row atoms (C, N, O, and F atoms) by adding a flexible Gaussian inter-electronic Hartree-Fock (HF) exchange integral to the LC scheme. We showed that LCgau-core-DFT functional could simultaneously achieve high accuracy in the reproduction of charge transfer and valence-Rydberg excitation energies, [2,3] as well.

In this research, we will show that LC2gau-DFT which has one more Gaussian inter-electronic HF exchange to LCgau-core-DFT can reproduce core excitations of both the 2nd- and 3rd-row atoms simultaneously with high accuracy, by considering relativistic effects in the calculations. Moreover, it will be presented that LC2gau-DFT can perform well for all types of excitations, as well as thermochemistry. A notable feature is the flexible inclusion of a short-range Gaussian inter-electronic HF exchange can improve the performance of DFT functional for various kinds of orbital energy calculations.

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(P-95)

Effect of Interfaces on Ion Transport Mechanisms in Block Copolymer Electrolytes: A Molecular Dynamics Study

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Block copolymer electrolytes (BCPEs) have been spotlighted for their impressive potential for battery applications since their ionic conductivity and mechanical stability improve simultaneously as the polymer chain molecular weight (M_W) increases [1,2]. The positive correlation between BCPE conductivity and M_W has been interpreted as a consequence of reduced volumetric portion of the domain interfacial zone which retards the ion movement [3,4]. However, experiments with low-M_W BCPEs implied complex interplay between various factors on the ionic conductivity in the finite-size regime that interface contribute significantly, represented by a temporary anticorrelation between M_W and conductivity [5]. In this study, we model lithium salt-doped poly(styrene-b-ethylene oxide) (PS-b-PEO) block copolymer electrolytes by molecular dynamics simulation in united-atom resolution. We capture a non-monotonic trend of BCPE ionic conductivity with respect to polymer chain M_W, attributing to the cross-over between decreasing vehicular ion mobility and increasing collective cation conduction mediated by local segmental motions as the polymer chain M_W increases. The dynamic heterogeneity at interfacial zone is represented by the local ion flux through the conducting PEO domain, indicating that the interfacial width is comparable to the size of a single cation coordination shell. Besides the consensus on the importance of interfacial ion retardation, our study shed new light on the predominance of polymer chain dynamics on the ionic conductivity of BCPEs.

Kyeong-jun Jeong completed his Ph. D. at the University of Wisconsin-Madison in 2020, under supervision of Prof. Arun Yethiraj. His doctoral research focused on characterizing soft matter self-assembly and phase behavior by molecular dynamics simulations. He is currently a postdoctoral researcher at POSTECH in Prof. Chang Yun Son's group.

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(P-96)

Investigating the Impact of Spin Contamination in Open-Shell Hartree-Fock DFT

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Hartree-Fock-DFT (HF-DFT) calculations have gained popularity for predicting chemical properties. However, spin contamination issue is intrinsic in open-shell calculations. By comparing two different open-shell Hartree-Fock (HF) densities across various density functional theory (DFT) functionals and density-corrected (DC)-DFT methods, we assess the impact of spin contamination on HF-DFT accuracy. Our results demonstrate that substituting the unrestricted HF (UHF) density with the restricted open-shell HF (ROHF) density significantly reduces the UHF-DFT error in cases with severe spin contamination. Building upon these findings, we refine the DC(HF)-DFT algorithm and recommend the use of ROHF-DFT as a viable solution for treating severe spin contamination. This research contributes valuable insights into understanding spin contamination effects and improving the accuracy of HF-DFT calculations within different DFT frameworks.

References

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In-situ XPS study of $Zn_xCd_{1-x}S$ Photocatalysts Depending on Irradiation Wavelength

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Photocatalysts are useful for various applications, including the conservation and storage of energy, wastewater treatment, air purification, semiconductors, and to produce high-value-added products. Herein, $Zn_xCd_{1-x}S$ nanoparticles (NPs) with different concentrations of Zn^{2+} ions were successfully fabricated. In-situ X-ray photoelectron spectroscopy (XPS) was performed to investigate the effect of the Zn vacancies on the irradiation wavelength for photocatalytic activity. Furthermore, wavelength-dependent photocatalytic degradation (PCD) activity of the $Zn_xCd_{1-x}S$ NPs was investigated using 2,5-hydroxymethylfurfural (HMF). We observed that the selective oxidation of HMF resulted in the formation of 2,5-furandicarboxylic acid (FDCA) depending on the irradiation wavelength for PCD. Herein, we used HMF to evaluate the photocatalytic activity of $Zn_xCd_{1-x}S$ NPs. In addition, we performed in situ X-ray photoelectron spectroscopy (XPS) measurements to investigate their wavelength-dependent photocatalytic activity as shown in Fig.1. Thus, this strategy is expected to contribute to the efficient design of novel photocatalysts for the selective oxidation of HMF.

References

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Modified rGO Nanocomposites with Enhanced Photocatalytic Activities

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Improving the photocatalytic properties of various types of metal oxides is becoming increasingly important in terms of environmental factors. Herein, various transition-metal-ion-doped reduced graphene oxide (rGO) samples were synthesized and characterized using X-ray absorption spectroscopy to investigate their electronic structures. Transition metal ion doping produced several defect structures at the oxygen functionalities of rGO nanocomposites. Such defect structures were well correlated with their photocatalytic activity; Cr@rGO and Fe@rGO exhibited decent activities among the tested rGO samples in the photocatalytic degradation of selective oxidation of 2,5-hydroxymethylfurfural. To test the environmental factors, cytotoxicity tests were performed by incubating the modified rGO with human skin cells; Fe@rGO was found to be the least toxic. Therefore, Fe@rGO nanocomposites displayed both enhanced photocatalytic activity and environment-friendly character as compared to the bare rGO, indicating that it is a plausible candidate for application in the petrochemical transformation of biomass without environmental concerns.

References

(P-99)

Temperature-dependent dioxygen reaction of an organonickel(II) complex

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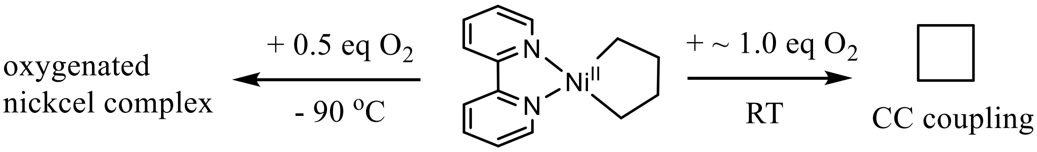
O_2 activation is prerequisite to mimic the reactivity of oxygenated intermediates in metalloenzymes such as compound I from cytochrome P450. The reductive O_2 activation by divalent Ni complexes are relative rare compared to Fe or Mn because of Ni's higher effective nuclear charge. Our group has found that organonickel complexes, Ni(II) complexes with carbon-based ligands, can perform fast O_2 activation efficiently. The Ni(II)(bipyridine)(1,4-butanediyl) complex displays different O_2 reactivities depending on the reaction temperature. At low temperature below # K, it reacts with O_2 in a binuclear manner with the stoichiometry of [Ni]:[O2] = 2:1 ratio, while at room temperature, the reaction requires 1 equivalent O_2. We have characterized the products and intermediates of the O_2 reactions with electronic absorption, ^{1}H NMR, and resonance Raman spectroscopies, and MS spectrometry. The analyses show that the O_2 reaction at a higher temperature gives a reductive eliminated product, while at a lower temperature, the reaction produced an oxygenated Ni complex which is a less reactive species even at room temperature. This study proposes that the lower-temperature reaction has higher chances to cleave the O-O bond for a full-extent O_2 activation.



SCHEME 1. O_2 reaction depending on temperature

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(P-100)

Quantitative analysis of solvation structure in organic liquid electrolytes using ATR-FTIR spectroscopy

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Organic carbonates are the primary electrolytes for lithium-ion batteries (LIBs), owing to their remarkable ability to dissolve lithium salts, high conductivity, and wide electrochemical window. Attenuated total reflection (ATR-FTIR) spectroscopy is commonly used to study the solvation structure of LIBs electrolytes.[1,2] However, ATR-FTIR presents challenges in the quantitative analysis due to its reliance on reflectance to generate spectra, which complicates the accurate application of Beer's law for estimating the difference in absorption coefficients between coordinated and non-coordinated carbonates. Furthermore, the penetration depth of the evanescent wave is longer at low wavenumbers, leading to an overestimation of coordinated carbonate concentration. Recently developed thin-cell IR spectroscopy allows for the measurement of high-absorbance samples with a path length of around 2 µm, offering a more accurate solvation structure with the transmission-type IR compared to ATR-FTIR.[3] However, applying this technique to spectroelectrochemical analysis to observe actual operating conditions is difficult. Thus, quantitative analysis with ATR-FTIR is essential. For conducting quantitative analysis with ATR-FTIR, Various ATR correction programs utilize the Kramers-Kronig relationship to make ATR spectra consistent with transmittance spectra. Nevertheless, the accuracy of corrected ATR spectra for solvation structure analysis compared to the thin-cell method remains uncertain. Here, we revisit ATR correction using the Kramers-Kronig relationship and highlight the differences in determining solvation structures between ATR-FTIR spectroscopy and thin-cell IR spectroscopy. Furthermore, we discuss approaches for accurately analyzing solvation structures using ATR-FTIR spectroscopy.

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(P-101)

Excited-state Reductive Elimination Reactions of High-valent Nickel Complexes

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A cross-coupling reaction is a highly valuable synthetic method for generating new bonds between hydrocarbon fragments by using transition metal catalysts. Palladium (Pd) catalysts have been extensively studied and utilized in industry. However, the high cost and limited availability of Pd and platinum (Pt) catalysts have led to recent investigations into nickel (Ni) catalysts. Ni catalysts can adopt various oxidation states that range from 0 to +4, exhibiting distinct reactivities compared to traditional Pd catalysts. Our previous research demonstrated that the C-C bond-forming reductive elimination (RE) activities of cycloneophyl ($CH_2C(CH_3)_2$-*o*-C_6H_4, hereafter CC) organonickel complexes are significantly variable by up to five orders of magnitude, depending on the oxidation state of the Ni center, Ni^{III} and Ni^{IV}, and their supporting ligands, 2,2'-bipyridine (bpy) and tris(2-pyridyl)methane (py_3CH). We found that the RE activity is determined by energy required to transfer charge from the carbon ligand to the metal center, and this C-to-Ni charge transfer (CT) is achievable by triggering LMCT transitions via visible light. The photo-induced RE activities were enhanced by 3 to 5 orders of magnitude compared to those of the ground-state RE reactions. In this study, we have prepared chlorinated high-valent Ni^{IV}(CC) complexes by adding 1 and 2 equivalents of chloride (Cl^-) to Ni^{IV}(bpy)(CC). They display distinct NMR spectra indicative of Ni^{IV}(bpy)(CC)(Cl) and Ni^{IV}(bpy)(CC)$(Cl)_2$ complexes. Building upon the previously found correlation between RE and LMCT transitions, we have excited the Ni^{IV} species with various visible lights and characterized reactivities to learn whether the C-C vs. C-Cl bond-forming RE reactions can be differentiated by excitation energies.

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(P-102)

Mechanical force transferred through DNA diblock: Scission of a specific covalent bond

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An ultrasound-induced bond cleavage on mechanopore, a weak bond along the polymer chains, is one of the main foci of polymer mechanical chemistry. To date, there are not many studies on the role of polymers, which are mechanical force carriers. Here we report precisely prepared DNAs as the mechanocarriers (MCs) instead of conventional polymers for the mechanochemical bond scission. For this study, a DNA-linker-DNA structure was designed in which a linker is located at the center and two DNA MCs are connected to both termini. We mainly used polymerase chain reaction to engineer DNA MCs and ultrasound as the mechanical force. The effect of DNA MCs was evaluated by changing the length, rigidity, and shape of DNA segments. We investigated to precisely control the bond scission by external force transmitted to the linker through DNA MCs.

References

(P-103)

Computational study of lipid-modified DNA: self-assembly and interaction with bilayer membrane

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An amphiphilic single-stranded DNA (U4T) contains four lipophilic uracil nucleobases at the 5'-end. The lipid-modified uracil bases aggregate forming spherical micelles with the hydrophobic core and DNA corona in an aqueous phase. In addition, U4Ts enhance cell permeability by the interaction between the uracil bases and lipid bilayer of a cell membrane. In this research, the aggregation of U4Ts and the U4T-bilayer interaction were studied by molecular dynamics (MD) simulations. We observed the aggregation of U4Ts by coarse-grained (CG) simulations and the interactions of U4Ts and dipalmitoylphosphatidylcholine (DOPC) bilayer by all-atom (AA) simulations. Consequently, U4Ts can aggregate into spherical micelles with excellent stability and are capable of docking onto cell membranes.

References

(P-104)

Calcium carbonate nucleation on polymer surface: A Molecular Dynamics Simulation Study

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The usage of polymers as a tool in the crystallization process is extensively investigated among the scientific community.[1] Despite this, the nucleation/crystal growth process and its relationship between the charged polymer is still not fully understood. A key factor in determining the nucleation near polymer surface is the electrostatic interaction through the symmetry-breaking boundaries. In this context, molecular simulations based on the reliable force field describing the interaction between charged polymer and ionic species are warranted to elucidate the physical origin of salt nucleation on polymer surface. In this study, we model the dendrimer of polyamidoamine (PAMAM) with calcium carbonate by performing classical molecular dynamics simulation in united-atom resolution. Our simulation results capture the nucleation of calcium carbonate on PAMAM surface, which is energetically favored by the electrostatic amine-ion interaction. Especially, our study shows that the hydrolysis of PAMAM near the surface of microparticle is vital to the precipitation of calcium carbonate on polymer surface. Our study shed light on the thermodynamic stability of precipitated calcium carbonate polymorph structure.

Sangmin Lee completed his B.S. degree in chemistry from POSTECH in 2022. He is currently a M.S.-Ph.D. integrated course student in the Department of Chemistry at POSTECH in Prof. Chang Yun Son's group.

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(P-105)

Computational investigation of stabilization mechanism of in-plane fractal patterns in two-dimensional MOF nanocrystals

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The guided etching of 2D Metal Organic Framework(MOF) nanocrystals is an important process to enable the creation of hierarchical and controlled pores, which lends itself to a wide range of applications such as molecular and bio-catalysts[1,2]. In this collaborative study, we evaluate thermodynamic and kinetic properties of a nano-sculpting strategy(NSS) introduced to engrave anisotropic *plus*-type and *fractal*-type patterns in a 2D MOF-5 nanocrystal, via <100> and <110> directional etching respectively.[3] We calculate the different energetic pathways and identify the major interactions influencing the process.

Using Molecular Dynamics (MD), we observed spontaneous substitution of a neutral 2D MOF-5 surface with solvent DMAc molecules. We also identified two distinct etching pathways, one thermodynamically preferred and other kinetic, for the subsequent removal of $[Zn_4O]^{6+}$ units in 2D MOF-5 surface. The thermodynamically preferred pathway for the <100> *plus*-type etching, proceeded through direct nucleation of the $[Zn_4O]^{6+}$, as concluded from Pulling Force methods using MD simulations. The kinetically preferred pathway was identified using DFT, while incorporating the effect of an implicit solvent. We recognized a two-step mechanism for the formation of <110> *fractal*-type pores through an exchange of metal-coordinating DMAc solvent molecules with Ethanol and subsequent dissolution of Ethanol-bound Zn nodes. The major interaction in this pathway was identified as that of the ethanol binding on to the $[Zn_4O]^{6+}$ unit.

Thus, the mechanisms investigated through computational methods were crucial in understanding and guiding the selective preparation of different types of pore patterns on the 2D MOF5 nanocrystal. This offers suitable strategies in future for the creation of holey and custom patterns on 2D nanomaterials for addressing new scientific challenges.

The presenting author, Akshay Gurumoorthi, is a graduate student in the Division of Advanced Materials Science, in POSTECH, South Korea working in the guidance of Prof. Chang Yun Son, Department of Chemistry and Division of Advanced Materials Science.

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(P-106)

Exploring the Role of Pioneer Transcription Factor FOXA1 in DNA Conformation: A Molecular Dynamics Simulation Study

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Forkhead box A1(FOXA1), is a transcription factor expressed in mammals. It plays a critical role in various tissues and organs, including the liver, pancreas, kidney, thyroid, and central nervous system. Additionally, it functions to regulate gene expression in breast tissue. the wing2 domain of FOXA1 is a common domain among transcription factors and plays an important role in structural stability and DNA binding by interacting with DNA. In the initiation process of the transcription FOXA1 can replace the Histon H1 protein during nucleosome disassembly. The interaction of the wing2 domain with DNA is important in the process of the nucleosome disassembly. Therefore, we performed atomistic molecular dynamics simulations of a 23-base pair DNA sequence with various FOX proteins, including FOXA1, FOXD3, and FOXA1 with a mutation. All simulations were performed up to 1 μs, and the distances between amino acid residues in the wing2 domain and bases in DNA were calculated to identify the major binding region between DNA and the proteins. Furthermore, the bending angle of DNA was calcuated in the presence of FOX proteins using the Curves+ program. We have observed that the wing2 domain plays critical roles in facilitating the bending of DNA.

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(P-107)

Surface-enhanced Raman Spectroscopy to track transport dynamics of hydrogen on graphene

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Exploring the atomic or molecular transport properties of two dimensional materials is vital to understand their inherent functions and, thus, to expedite their use in various applications. Herein, a surface-enhanced Raman spectroscopy (SERS)-based in situ analytical tool for the sensitive and rapid monitoring of hydrogen transport through graphene is reported. In this method, a reducing agent, which can provide hydrogen species, and a Raman dye self-assembled on a SERS platform are separated by a graphene membrane, and the reduction of the Raman dye by hydrogen species transferred through graphene is monitored with SERS. For validating the efficacy of our method, the catalytic reduction of surface-bound 4-nitrothiophenol by sodium borohydride was chosen in this study. The experimental results distinctly demonstrate that the high sensitivity and rapid detection ability of SERS can allow the effective analysis of the hydrogen transport properties of graphene.

References

(P-108)

Computational investigation of conformational change and material utilization of the G-quadruplex : From the perspective of the central cation

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Single-stranded nucleic acids have high flexibility and can be folded in various ways. Recent evidence suggests G-quadruplex (G4) involvement in numerous key genome functions. G4 can form various conformations in one sequence depending on different conditions, and there are over 700,000 regions exist that could be G4 in the human genome. Experiments identified the structural polymorphism of G4 sensitively responding to the changes in salt environment, but understanding detailed folding mechanism of this process is challenging due to the limited resolutions. Cations located in the core of G4 and has a great influence on stability, are the most investigated factor for the conformation of G4, but the detailed mechanism of ion-dependent conformational change of G4 is still illusive. It is also noteworthy that due to the special structure that resembles the ion channel protein, G4 has the potential to be a candidate for biomimetic ion channels. Here, we performed all-atom molecular dynamics (MD) simulation to check the stability of the G4 structure affected by the core-forming cations, using two representative crystallographically resolved G4 structure with same sequence but different cations. Using an enhanced sampling method, we sampled the conformational space for the interconversion of the G4 structure upon Na^+ and K^+ to identify molecular features that play a key role in the stability of the G4 structure and analyze the energy preferences for conformational changes in folding process. We also have identified the potential of G4 as an artificial channel by performing MD simulation showing that negatively charged DNA is stabilized inside the hydrophobic cell membrane through central cations and backbone neutralization with alkyl groups.

Juhwa Lee is currently a graduate student at Pohang University of Science and Technology, pursuing a master's degree under the supervision of Prof. Chang Yun Son. Her research focused on the investigation of structural properties and conformational changes of biomolecules by molecular dynamics simulations.

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(P-109)

Mechanistic study on N-dealkylation of a Co(II) complex

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Oxidative *N*-dealkylation is a key step in the metabolism of xenobiotics, catalyzed by cytochrome P450 family enzymes. Fe catalysts have been majorly developed to mimic the enzymatic *N*-dealkylation reaction, while divalent Co species have been less considered due to their relatively high effective nuclear charge and thus lack of O_2 activating power. Recently we have discovered that a Co(II) complex with the macrocyclic tetradentate N4 ligand can activate O_2 in high-pH aqueous media, displaying long time-scale (>100 hours) variations in electronic absorption and magnetic circular dichroism spectra. The intermediates and product of the reaction have been characterized with ESI-MS, NMR, resonance Raman, and IR spectroscopies. Their structural candidates have been assessed with density functional theory computations. These analyses have revealed that the O_2 activation in aqueous media can result in the *N*-dealkylation of the tertiary amine ligand. The mechanistic study suggests that the aqueous media can play a major role in promoting the *N*-dealkylation reaction by interplaying with ROS species.

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(P-110)

Advancements in AI-assisted Reaction Planning

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In the recent series of studies, we showcase the utilization of atom environments, neural machine translation (NMT), and a novel tokenization scheme to enhance prediction accuracy in reaction planning. We developed RetroTRAE, a single-step retrosynthesis prediction method that uses atom environments as chemically meaningful descriptors to guide reaction route prediction. This approach circumvents the issues associated with SMILES-based translations, demonstrating improved performance over other NMT-based methods, with a top-1 accuracy of 61.6% when including highly similar analogs. This new method emphasizes molecular fragments over SMILES strings for chemical reaction representation, leading to more robust predictions and resolving issues of invalid SMILES strings generation. In addition, we address tokenization, a critical step in natural language processing (NLP) that impacts prediction quality. The proposed atom-in-SMILES tokenization reduces ambiguities present in generic SMILES tokens and mitigates token degeneration, thereby improving the quality of SMILES sequences generated by AI-based chemical models. Our studies provide an expansion in the fields of NLP, NMT, and AI-assisted reaction planning, emphasizing the potential of a substructural approach and atom environments for improved prediction performance in chemical informatics.

References

(P-111)

Guided molecular generation via fragment-based incorporating with physico-chemical properties

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Recent research has established the translation of molecular fingerprints into their original molecular structures as a viable strategy for the generation of target molecules. This research extends our prior work, where we successfully reconstructed molecule, SMILES representations, from their fingerprintswith a high degree of accuracy [1]. This was further complemented by the development of the atom-in-SMILES tokenization [2] scheme, which resulted in enhanced prediction quality and more effective production of SMILES sequences from AI-based chemical models.

The present study proposes a novel method for the generation of target molecules, which involves the integration of molecular fingerprint features and physico-chemical properties. This approach utilizes the inherent interpretability of fingerprint features, thereby guiding the generation of molecules exhibiting specified properties. The proposed methodology has the potential to streamline drug discovery and materials design processes through its facilitation of efficient and precise molecule production.

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(P-112)

Combination Plasmonics: A Quest for Nanoparticle Assemblies with Maximum Surface-Enhanced Raman Scattering

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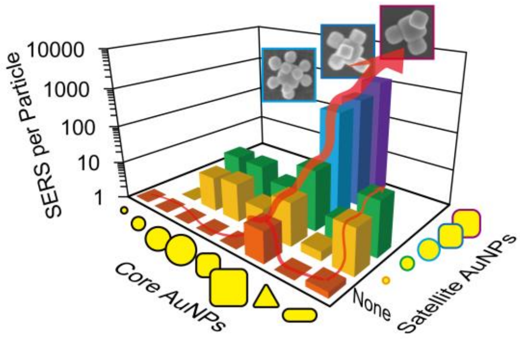
Plasmonic nanoparticles exhibit unique properties that distinguish them from other nanomaterials, including vibrant visible colors, generation of electric fields, production of hot charge carriers, and localized heat emission. These properties are particularly enhanced in the narrow nanogaps formed between nanostructures. Therefore, creating nanogaps in a controlled fashion is the key to achieve a fundamental understanding of plasmonic phenomena originating from the nanogaps and develop advanced nanomaterials with enhanced performance for diverse applications. One of the most effective approaches to create nanogaps is to assemble individual nanoparticles into a clustered structure. In this study, we present a fast, facile, and highly efficient method for preparing core@satellite (CS) nanoassembly structures using gold nanoparticles of various shapes and sizes, including nanospheres, nanocubes (AuNCs), nanorods, and nanotriangular prisms. The sequential assembly of these building blocks on glass substrates allows us to obtain CS nanostructures with a 100% yield within 4 h. Using nine different building blocks, we successfully produce sixteen distinct CS nanoassemblies and systematically investigate the combinations to search for the highest Raman enhancement. As a result, we discover that the surface-enhanced Raman scattering (SERS) intensity of AuNC@AuNC CS nanoassemblies is two orders of magnitude larger than that of other CS nanoassemblies. Theoretical analyses reveal that the number of molecules in the interfacial region, as well as the intensity and distribution of the electric field induced in the nanogaps by plasmon excitation, collectively contribute to the unprecedentedly large SERS enhancement observed for AuNC@AuNC. This study not only presents a novel assembly method that can be extended to produce many other nanoassemblies, but also identifies a highly promising SERS material for sensing and diagnostics through a systematic search process.



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(P-113)

Facile synthesis of Pd@Pt core-shell nanodendrite for boosting methanol oxidation reaction

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The single-pot production of Pd@Pt core–shell structures is a promising approach as it offers high surface area, catalytic capability, and stability [1]. In this work, we established a single-pot process to produce Pd@Pt core–shell nanodendrites with uniform shape and tunable size and composition for optimal electrocatalytic activity. Pd@Pt nanodendrites with different compositions were synthesized by adjusting the ratios of Pd and Pt precursors in an aqueous environment using cetyltrimethylammonium chloride, which acted as both the surfactant and the reducing agent at an elevated temperature (90 ℃)[2]. The synthesized Pd5@Pt5 nanodendrites showed exceptional electrocatalytic performance toward the methanol oxidation reaction compared with other compositional Pd@Pt nanodendrites and conventional Pt/C electrocatalysts. In addition, Pd5@Pt5 nanodendrites exhibited good CO tolerance owing to their surface structure and the synergistic effect between Pt and Pd [3,4]. Meanwhile, nanodendrites with a Pt-rich surface and high-index facets provided exceptional catalytic active sites [5]. Compared with the conventional Pt/C electrocatalyst, the anodic peak current obtained by Pd5@Pt5 nanodendrites was 3.74 and 2.18 times higher in terms of mass and electrochemical active surface area-normalized current density, respectively. This approach offers an attractive strategy to design electrocatalysts with unique structures and outstanding catalytic performance and stability for electrochemical energy conversion.

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(P-114)

Exploring the Effects of Cytosine Methylation in CpG Islands on DNA Conformation: Molecular Dynamics Simulations

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In carcinogenesis, preneoplastic cells transform into tumor cells, grow into carcinoma, and are eventually metastasized to other organs via blood vessels. The metastasized tumor cells can grow back in the metastasized organ to cause tumors [1]. Many studies have reported that the methylation of the 5th carbon in the cytosine residues in CpG islands of DNA in human cancer cells may be closely related to the cancer and that the demethylation of 5-methylcytosine may be used as a cancer therapy [2,3]. However, how the methylated cytosine in CpG islands would affect normal DNA to cause cancer has not been studied extensively up to now.

In this study, the atomistic molecular dynamics simulations are used to study DNA conformational changes according to the degree of methylation of the cytosine residues in a CpG island. We mimic the CpG island with 16 base pairs that only consist of C and G nucleic acids. Then, we randomly methylate cytosine residues. The simulations are independently conducted with or without an external electric field. The presence of an electric field leads to a broader distribution of DNA end-to-end distances. Additionally, the DNA methylation makes DNA shorter, resulting in a narrower distribution of end-to-end distances.

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Force Field dependent structural and dynamical properties in lithium/ionic liquid electrolytes

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Room temperature ionic liquids (RTILs) have been investigated for their impressive potential as electrolytes in lithium-ion batteries due to their non-volatile and non-flammable properties, which contribute to the development of safe electric storage. However, experimental and simulation studies have reported a negative transference number for lithium, indicating that the lithium ion moves in the opposite direction of the electric field due to the formation of lithium-anion clusters [1,2]. This phenomenon can directly reduce the performance of lithium-ion batteries. Therefore, understanding the correlation motion and clustering behavior is crucial for enhancing battery performance. In this study, we employed molecular dynamics to model lithium salt-doped ionic liquid electrolytes, particularly [EMIM][BF4]. We developed a transferable and predictable ab-initio force field for the lithium ion and compared our simulation results with other force field models. The clustering behavior between the BF4 anion and the lithium ion was found to be highly dependent on the force field, in contrast to the results of simulations using neat ionic liquids. Moreover, the dynamical properties varied depending on the force field, and the polarizable model, especially our model, accurately captured the dynamical properties compared to experimental results. Our findings underscore the importance of an accurate force field model for the lithium/ionic liquid system, and the understanding of cation-anion correlation motion opens up new avenues for designing high-performance lithium-ion batteries.

Seungwon Jeong is a graduate student enrolled in M.S and Ph.D. integrated course at POSTECH under the supervision of Prof. Chang Yun Son. His research is focused on lithium-ion electrolytes, polymer electrolytes, machine learning-based potential through molecular dynamics simulations.

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