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POSTER ABSTRACTS

(P-1)

Investigation of the Role of TiO_2 Underlayer in the Anodic Potential Shift of the Onset Potential in Hematite (α-Fe_2O_3) Photoanode

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Improvements in the performance of photoelectrodes in photoelectrochemical (PEC) systems are typically associated with cathodic shift of onset potential and enhancement of photocurrent density. However, our investigation into hematite photoanode with a TiO_2 underlayer revealed a notable increase in photocurrent density alongside an unexpected anodic shift of onset potential. This suggests that, particularly at lower voltages, the TiO_2 underlayer plays a significant role in Fermi level pinning. Our findings indicate that hematite with a deposited TiO_2 underlayer exhibits high carrier density and low photovoltage. However, back recombination was confirmed to be three times slower than that of bare hematite, confirming that the TiO2 underlayer functions as a blocking layer, as is known. We plan to conduct follow-up research on relieving Fermi level pinning through methods such as treatment of the interface between TiO_2 and hematite.

(P-2)

Exploring Photodissociation and Roaming dynamics in Solution: Insights from Iodobenzene and Diiodobenzene

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Alkyl halides and aryl halides serve as ideal systems for studying bond-breaking dynamics. Photodissociation of aryl halides containing heavy halogens, such as iodobenzene (PhI), exhibits more complex dissociation dynamics compared to alkyl halides. While the bond dissociation of PhI in the gas phase has been extensively studied [1–2], research on its photodissociation dynamics in solution is limited due to the low signal-to-noise ratio in solution-phase experiments. Additionally, high computational costs for theoretical calculations have resulted in limited investigations into the excited state dynamics of diiodobenzene (PhI_2). By employing time-resolved spectroscopy, electronic structure calculations and molecular dynamics simulations, we comprehensively explored the photodissociation dynamics of PhI and *ortho*-, *meta*-, and *para*-diiodobenzene (*o*-, *m*-, and *p*-PhI_2). Our results indicate that in acetonitrile, after 267 nm photoexcitation, PhI rapidly dissociates into Ph• and I•, which then recombine geminately to form an isomer, *iso*-Ph···I. Conversely, *o*- and *m*-PhI_2 undergo the formation of the isomer, namely *iso*-PhI···I, in acetonitrile following 267 nm photoexcitation. Notably, it is expected that after photoexcitation of *o*-PhI_2, *iso*-PhI···I form quickly through the reorientational motion of the iodine atom in the long-range region, a process known as roaming. Conversely, *iso*-PhI···I form more slowly due to the diffusion of the iodine radical in the solvent cage after photodissociation of *m*-PhI_2. Using theoretical methods, it is confirmed that photodissociation of PhI mainly occurs through the triplet states, and all the possible isomers of PhI and PhI_2s are stable in the triplet state in acetonitrile. This study provides significant insights into the complex bond-breaking processes in aryl halides, highlighting the roles of roaming and diffusion processes that may follow bond cleavage in solution.

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(P-3)

Illuminating the Mechanism of Chan–Lam C–N Coupling with Iridium Photocatalyst: A Time-resolved X-ray Absorption Spectroscopy Study

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Transition metal dual catalysis is emerging as a powerful strategy in organic photoredox chemistry.[1] When photoredox catalysis is combined with metal catalysis, it enables reactions even under mild conditions with substrates that are otherwise unreactive under metal catalysis alone. A representative system of this type is the copper-catalyzed C–N coupling within the Chan–Lam coupling framework with iridium-based photoredox catalysis. We applied time-resolved X-ray absorption spectroscopy (XAS) to gain insights into the Chan–Lam C–N cross-coupling of anilines and aryl boronic acids enabled by an iridium photocatalyst.[2] XAS provided a window into changes in the coordination chemistry and oxidation state of the copper and iridium complexes. Analysis of the copper K-edge data indicates redox participation of the copper catalyst.[3] Meanwhile, the iridium L_3-edge shows clear spectroscopic signatures of photoexcited state speciation.[4] This work underscores the efficacy of time-resolved X-ray spectroscopic techniques in elucidating mechanisms within dual catalytic reactions, encouraging further studies aimed at capturing short-lived intermediates. A deeper understanding of the synergistic interactions between catalysts will guide the design of new cooperative catalytic systems for photoredox synthesis.

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(P-4)

Unveiling the Local Structure of Liquid Water via X-ray Spectroscopy Simulations Employing Multiconfigurational Wave Function Theory

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X-ray absorption spectroscopy (XAS) has emerged as a powerful tool for investigating the electronic and structural properties of molecules. By manipulating photon energy to excite core electrons, it offers element-specific insights into materials and finds broad applications in various fields of chemistry, such as catalysis, materials science, and biochemistry.[1,2] Within this framework, the XAS spectra of water have been widely investigated, serving as a paradigmatic example. The oxygen K-edge XAS spectrum of liquid water displays prominent peaks at specific energy values: the pre-edge (~535 eV), main edge (~538 eV), and post-edge (~541 eV), corresponding to confined intramolecular excitons, excitons localized within the coordination shell, and the delocalization spanning distant water molecules, respectively.[3] Furthermore, the hydrogen bonding network has been identified as a key player in shaping and modulating the energy levels present in the XAS spectrum of water, yielding valuable insights into its intricate fine structure.[4,5] This relationship is still not fully understood although it is indispensable for obtaining structural information about water systems. In an effort to improve this description, we develop a computational protocol that combines molecular dynamics (MD) simulations and accurate multireference (MR) calculations to calculate the XAS spectra of water, with the goal of enhancing our understanding of the absorption spectrum-water structure relationship and improving the description of the XAS spectra of water.

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(P-5)

Global warming potential estimation of alternative semiconductor process gases: a computational approach

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The Global Warming Potential (GWP) is a relative measure that indicates the potential impact of a substance on global warming in the atmosphere, using the effect of carbon dioxide as a standard, set at 1. The estimation of GWP is determined by various factors, primarily the lifetime in the atmosphere and the absorption cross-section for solar radiation. GWP has been calculated for several greenhouse gases, and efforts are being made to minimize the use and emission of substances with high GWP. As an example of these efforts, the need to replace gases such as nitrogen trifluoride (NF_3), which are used for and cleaning in the semiconductor manufacturing process is being proposed. This substance has very high GWP value, which are estimated to be around 17,400 in 100 year horizons. Therefore, research is actively undergoing to replace these substances with others. However, calculating the GWP of these new substances can be challenging due to obstacles such as the complicacy of tracking them in the global atmosphere and predicting their lifetimes. In this study, we have several goals utilizing computational chemistry methods, and we have obtained information about the vibrational absorption spectra and the transition states of decomposition reactions for several substances, such as Carbonyl fluoride (COF_2) and NF_3. Using this information, we derive the infrared absorption cross-section under solar radiation, and the rate constants. We then compare these results with existing experimental and computational data [1-4], and conduct furthermore comparisons with some substances for which the GWP is known. Ultimately, this study aims to estimate and collect the GWP of the target gases, and additionally, it seeks to establish a theoretical methodology for estimating the GWP values of various substances.

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Two Liquid State Model on Water Anomalous Properties

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Abstract

Water is a unique substance which shows various anomalous properties distinct from other liquids. Fundamental understanding of anomalous properties of water is still a mystery and a controversial topic.[1] One promising scenario is the Poole's second critical point hypothesis in which the second critical point is the liquid liquid transition critical point between two liquid states of water (HDL and LDL) in a supercooled region, where these liquid states of water were distinguished through x-ray and vibrational spectroscopy as well as molecular dynamics simulation.[2-4] In this study, molecular dynamics simulation was performed at various temperature using TIP4P2005 water model and structural analysis was made to define and analyse LDL and HDL population. From molecular dynamics simulation, HDL and LDL population varies according to temperature in which can make contribution to the water density anomaly. Moreover, it was shown at ~230K that there is a crossing point between HDL and LDL population which is surprisingly the region where thermodynamics response functions such as thermal expansion coefficient, isothermal compressibility and heat capacity are showing a distinct behaviour from other liquids.[5] Hence, it is anticipated that the fluctuation of these two liquid state populations can play an important role on the anomalous properties of water.

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(P-7)

Unraveling the Interplay of Temperature with Molecular Aggregation and Miscibility in TEA-Water Mixtures

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Within the phase diagram of binary liquid mixtures, a distinct miscibility gap is observed, indicating the coexistence of two immiscible liquid phases at equilibrium, a phenomenon known as liquid-liquid phase separation. This behavior is prominently influenced by temperature, serving as a critical parameter in modulating phase behavior. These encompass critical temperatures such as the lower critical solution temperature (LCST) [1] and upper critical solution temperature (UCST) [2]. In this work we conducted molecular dynamics (MD) simulation, graph theoretical analysis [3] and spatial inhomogeneity measurement [4]. Based upon the combined study, our objective is to establish a relationship between aggregation behavior and LCST phenomena in TEA-water mixtures [5]. It was shown that TEA molecules exhibit a propensity to interact with water, yielding a homogeneous solution at lower temperatures. However, upon temperature elevation TEA aggregates prefer to self-associate, diminishing their interaction with water and facilitating the formation of two distinct liquid phases in the binary mixture. Spatial inhomogeneity measurement suggests the existence of water compatible TEA aggregates while maintaining a one phase mixture at lower temperatures. At higher temperatures, water-incompatible TEA aggregates lead to a phase separation behavior. The ongoing investigation into temperature-induced molecular aggregation behavior is expected to enhance our crucial understanding of phase behavior in binary liquid mixtures, incorporating phenomena such as UCST, LCST, and reentrant phase behavior.

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Morphological structure in molecular aggregation and phase behavior in aqueous binary liquid mixtures

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The self-associated aggregation behavior of solute molecules in aqueous solutions has been continually studied from many decades and is still a center of attraction for many scientists because it plays a key role in solution properties, such as miscibility and liquid-liquid phase separation phenomena [1-3]. We intended to demonstrate the concentration dependent aggregation behavior by performing molecular dynamics (MD) simulation with graph theoretical analysis and measuring spatial inhomogeneity (*h*-value) in three binary aqueous mixtures [3]. Tetramethylurea (TMU), 1,2-dimethylhydrazine (1,2-DMH), and Tetrahydrofuran (THF), which show different phase behavior in water, are studied at 350 K temperature with various concentrations. At lower concentration, all of the cosolvent molecules form homogeneous solutions with water, even when they exhibit inhomogeneous distribution at microscopic level. However, as concentration increases, TMU makes mutually associated aggregates with concentration dependence in *h*-value, indicating homogeneous distribution with increasing concentration [4]. In the graph theoretical analysis, it was shown that 1,2-DMH tends to make spatially extended aggregates, which are well intertwined with water hydrogen bond network, regardless of concentration [2]. In case of THF-water mixtures, it undergoes phase transition from one phase to two phases, which results in higher *h*-value, as the concentration increases. Overall, these findings provide a clear perspective on the molecular level structural changes of cosolvent molecules, and the study on concentration dependence in molecular aggregation behavior is critical for understanding the phase behavior of binary liquid mixtures.

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Molecular Aggregation Behavior and Freezing Point Depression in DMSO-Water Mixture

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Understanding the cryochemistry and cryobiology of aqueous cryoprotectants at ultralow freezing temperature has posed challenges to the scientific community as the mechanism by which they protect biological samples is still inconclusive [1]. To address these challenging issues, cryoprotectant molecule, DMSO have been investigated using MD simulations and graph theoretical analysis [2] meticulously to predict the plausible cryomolecular mechanism of DMSO at 213K and 298K. The water O-O radial distribution function (RDF) analysis in 0.33 mole fraction of DMSO-water system suggested that pure water O-O RDF representing 298K overlaps with mixture water O-O RDF at 213K. It implies that water structure is preserved in the 0.33 mole fraction of DMSO-water mixture than other two concentrations at 213K [3]. Among three concentrations chosen, 0.33 mole fraction mixture projected significant 1DMSO:2H_2O H-bond interactions, which appear to be responsible for anti-icing cryoprotective mechanism. The water diffusion coefficient computed in three DMSO-water concentrations fits reasonably well with published data [4]. The molecular insights obtained from MD simulations and graph theoretical analysis of DMSO-water mixture clarify why DMSO is the preferred cryoprotectant over alternative options for cryopreservation of biological samples. However, integration of computational and experimental studies are required to elucidate molecular mechanism of H-bond making and breaking in the aqueous cryoprotective DMSO-water mixture at ultralow freezing temperatures.

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(P-10)

Alkali halide cluster anion generation through laser desorption & Photodissociation and Electron attachment dynamics

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A newly designed laser desorption apparatus makes it possible to study the alkali halide and its cluster anions in the gas phase. For the first time, the intensity of laser-desorbed anions is enhanced by combining laser desorption with a filament ionizer. It is attached to a Wiley-Mclaren TOF mass spectrometer and a photoelectron velocity map imaging (VMI) apparatus.

Secondary electrons from the filament interact with the vaporized neutrals to produce anions. These anions are injected into the Wiley-Mclaren TOF mass spectrometer and mass selected. Mass-selected anions are transferred to the VMI apparatus and interact with the pulsed (ns/ps/fs) laser beam. The photoelectron signal is then collected by an MCP detector.

Alkali halide molecules such as NaCl, NaI, and KI have sufficient dipole moments in excess of 9D so that their anions have a dipole-bound state (DBS). The DBS anions are considered to be the "doorway" for electron attachment processes. For the alkali halide cluster anions such as $\mathbf{I^- \cdot \boldsymbol{Na}I}$, the alkali halide (NaI) and the cluster (I-) can be dissociated by a multiphoton dissociation process. In the course of dissociation, an electron can be released from I- and transferred to the alkali halide. Alkali halide anion may have a potential to be generated by DBS. In the study of these anions, spectroscopic information can prove the photodissociation and electron attachment dynamics in the alkali halide cluster anions.

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(P-11)

Preferential leaching of chromium from nickel-based alloys in molten KCl salt at high temperature

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The corrosion behaviors of nickel-based alloys 600, 617, and Hastelloy N in molten KCl salt at 800 ºC for 100 h under an argon atmosphere were investigated using field emission scanning electron microscopy (SEM), energy dispersive X-ray fluorescence (XRF), field emission electron probe microanalyzer (EPMA), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). In the SEM images, pits on the surface of all alloys were observed after corrosion experiments. By comparing XRF data obtained before and after the corrosion tests, it confirmed that the relative content of Cr element in all alloys was significantly reduced under molten KCl salt. In addition, cross-sectional EPMA mapping data measured after corrosion experiments showed that Cr element was predominantly leached along the grain boundaries in all alloys. Moreover, we performed ICP-AES analysis for solid KCl melt obtained after the corrosion experiments to determine the elements leached from the alloys. As a result, Cr element was remarkably detected in solid KCl melt compared to the other elements. On the basis of our analytical results, we verified that the corrosion of alloys 600, 617, and Hastelloy N in molten KCl salt occurred due to preferential leaching of Cr element along grain boundaries, forming pits on their surfaces.

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Reaction behavior of cyclohexanol on Ge(100) surface

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The reaction behavior of cyclohexanol on a Ge(100) surface is investigated using high-resolution photoemission spectroscopy (HRPES) and density functional theory (DFT) calculations. The O 1s spectra obtained from the adsorption of cyclohexanol on the Ge(100) surface show a peak at 530.8 eV related to a neutral oxygen atom. In addition, we observed the two distinct peaks at 284.5 and 285.5 eV in the C 1s spectra, which are associated with the neutral carbon atoms and a carbon atom adjacent to the oxygen atom in cyclohexanol adsorbed on the Ge(100) surface, respectively. Through the analysis of HRPES data, we suggest that cyclohexanol reacts with the Ge(100) surface via O-H dissociation, with the formation of a dissociation adduct. Furthermore, DFT calculations indicate that the on-top dissociative pathway has a lower activation barrier and transition-state energy than the intradimer row dissociative pathway. On the basis of our HRPES and DFT results, we identified that the on-top dissociative mechanism is more favorable than the other when cylcohexanol is adsorbed on the Ge(100) surface.

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Investigation of the Effect of Passivation on the Charge Transfer from $MAPbI_3$ to Electron Transport Layer Using a Heterodyne Transient Grating Spectroscopic Technique

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We fabricated $MAPbI_3$ perovskite thin films with ZnO on a glass substrate, in which a passivation layer (Phenethylammonium iodide (PEAI); *p*-methoxyphenethylammonium iodide (CH_3O-PEAI); 2-methoxyethylammonium iodide (MEAI)) was inserted between two layers. In order to understand the effect of the insertion of each passivation material on the transfer efficiency of the photo-generated electrons from $MAPbI_3$ to ZnO, we observed the near-field heterodyne transient grating (NF-HD-TG) responses of each film and investigated the component arising from the recombination of the trapped electrons at the ZnO surface. Based on the accelerated recombination between photo-generated holes remaining in the $MAPbI_3$ layer and surface-trapped electrons in ZnO and the increase in the number of the trapped electrons in ZnO when either CH_3O-PEAI or PEAI was applied, we successfully revealed that the charge transfer efficiency was enhanced by the insertion of the passivation materials including a benzene ring stabilizing the defect states. Particularly, it was demonstrated that CH_3O-PEAI showed the highest increase in the charge transfer efficiency, which could be attributed to the high electron density in the benzene ring, resulting from the existence of the electron donating group, CH_3O, and its role in the effective transition from 3D to 2D perovskite phases.

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Investigation of Charge Transfer Efficiency in $MAPbI_3$ Perovskite Solar Cells with Various Copper-based Hole Transport Materials Using Near-Field Heterodyne Transient Grating Spectroscopy

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In this study, we fabricated different types of $MAPbI_3$ perovskite solar cells, in which various copper-based hole transport materials (CuSCN, CuO, and CuS) were inserted as the hole transport layer and investigated the effect of each treatment on the charge transfer efficiency using Near-Field Heterodyne Transient Grating Spectroscopy (NF HD-TG). [1] In the previous study, we investigated the effect of CuSCN as the HTL on the hole transfer efficiency in perovskite solar cell [2-3] and observed the retardation of recombination, arising from the surface-trapped electrons in the ETL with the holes transferred to CuSCN, the HTL. In this study, based on the results we obtained in the former study, we successfully confirmed that charge transfer from the perovskite layer was significantly influenced by varying the HTL.

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(P-15)

Introduction of Nickel Ferrite ($NiFe_2O_4$) for Resolving Anodic Shift Caused by TiO_2 Blocking Layer in Hematite (α-Fe_2O_3) Photoanode.

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In hematite photoanodes that could be utilized for photo-electrochemical (PEC) water splitting, it has been known that the insertion of a TiO_2 blocking layer that retards the back recombination often results in an anodic shift of the onset potential in the current density versus applied voltage curve. [1] To address this issue, in this study, we introduced a nickel ferrite ($NiFe_2O_4$) layer, which was previously found in our group as a blocking layer. [2] We demonstrated that the hematite photoanode with both $NiFe_2O_4$ and TiO_2 layers not only maintained the high current density but also exhibited a cathodic shift in the onset potential, compared to those in hematite with the TiO_2 layer. Using various electrochemical and time-resolved spectroscopic techniques, we could reveal the origin of the improved performance with the insertion of the nickel ferrite layer.

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(P-16)

Chemically driven dissipative oligoesterification

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A primary characteristic of biopolymers, such as nucleic acids and proteins, is their ephemerality; they are constantly synthesized and degraded in living cells. The synthesis of biopolymers requires the activation of their monomeric building blocks, while their hydrolytic degradation into monomers is spontaneous. These natural dissipative systems have inspired the design of artificial counterparts utilizing various types of molecules and energy sources. However, artificial systems that produce transient oligomers with specific directionality, akin to biopolymers, largely remain unreached. In this study, we present a comprehensive kinetic investigation of the carbodiimide-driven transient oligomerization of a hydroxybenzoic acid derivative and the construction of a dynamic oligomer library. We anticipate that the discovery of a new transient oligomer with directionality and its corresponding chemical fuel may offer a unique opportunity to design dissipative systems capable of emulating sophisticated biological processes.

(P-17)

Dynamical Siumulation of Quantum Logic Gates based on Electronic Structure Calculations of Semiconductor Quantum Dots

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Gate-defined semiconductor quantum dots (QDs) form a useful platform for quantum computing due to their high controllability and fidelity in qubit operations. Computational studies on the electronic structure of the QDs may facilitate the discovery of new manipulation schemes for realizing efficient quantum logic gates. In this work, we have performed full configuration-interaction (FCI) calculations on coupled singlet-triplet (–) (S-T_-) qubits to study how the electronic energies and Hamiltonian parameters depend on the structure of the QD system. The QDs were modeled as truncated 2-dimensional harmonic potentials, and the electronic integrals were calculated by combining Fock-Darwin (F-D) states with the generating function method. [2] The structure of the QD systems was tuned to exhibit tunnel couplings observed in the experiments. For both gallium (Ga) and silicon (Si) matrix, it was observed that the behavior of S-T_- qubits was not significantly affected by the size of the basis set, in terms of the avoided crossing, exchange couplings, and qubit energy gaps. In the future, we plan to use such computational capability to perform dynamical simulations of quantum logic gates employing S-T_- (singlet-triplet) qubits. [3]

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(P-18)

Chemical fluctuation produced by stochastic switch with competitive versus non-competitive inactivation: A pivotal role of active state duration variability

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Advances in single-molecule experimental technology allow the observation of heterogeneity in various enzyme activities beyond the ensemble measurement. The previous theoretical approaches have succeeded in explaining turnover time distribution and its randomness parameter that classical reaction kinetics formulation cannot describe. However, there is a lack of theoretical framework to clearly explain the experimentally observed correlation between turnover times, which is beyond the scope of the renewal assumption for turnover times. In this work, we present a general matrix formulation enabling a quantitative explanation of the turnover time correlation of the on-off process, one of the central quantities characterizing non-renewal transcription processes. Using our theory, we derive a general relationship of the turnover time correlation and burst size with the transition matrix governing the transcription process, providing a physical insight into the profile of the turnover time correlation function and burst size distribution.

(P-19)

Prediction of DNA Absorption Spectrum Using Three-Base Nearest-Neighbor Model

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Quantification of DNA is a crucial aspect in biological and chemical research. A common method for DNA quantification involves using the extinction coefficient and absorbance parameters from the absorption spectrum of a specific DNA sequence. Monophosphate nucleotides absorb ultraviolet light with a peak around 260 nm due to the aromatic rings in their nitrogenous bases. While methods based on the extinction coefficient have been reported for some time, innovations in this area have been sparse. Here, we introduce an absorption spectra prediction tool tailored for single-stranded DNA, utilizing its extinction coefficient with a three-sequence nearest-neighbor model. This model extends the conventional nearest-neighbor approach by considering three sequence bases instead of two, simplifying the calculation of the extinction coefficient. Our proposed model demonstrated high prediction accuracy when compared with both experimental data and predictions from established models. To enhance accessibility, we provide simple, user-friendly Python code for easy implementation of this model. Our findings offer a framework for further advances in DNA quantification, providing a valuable tool for diverse applications in molecular biology and biotechnology.

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(P-20)

Photochemical Dynamics of S-Nitroso-Mercaptoethanol probed by Femtosecond Time-Resolved IR Spectroscopy

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In this study, we utilized femtosecond time-resolved infrared spectroscopy (TRIR) to analyze ultrafast dynamics occurring in photochemical reactions. The primary focus was on the reaction mechanisms of photoactive nitric oxide (NO) donors, which have potential biomedical applications.[1] We investigated the reaction mechanisms occurring over a range of hundreds of femtoseconds to tens of microseconds by examining the vibrational modes of intermediates, reaction rates, and absorption coefficients of each vibrational mode.

S-Nitrosothiol (RSNO), produced by nitrosylation of thiols, plays a crucial role in transmitting and regulating NO signals in biological systems.[2] 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.

During the analysis, we actively utilized computational chemistry and reaction kinetics to identify candidate intermediate structures while maintaining thermodynamic spontaneity and kinetic consistency. By studying the dynamics of various molecules, we resolved discrepancies between experimental and computational results and explained reaction rates using transition state theory (TST). We conducted an in-depth kinetic study of S-nitrosothiol (RSNO) by calculating its ground and excited state potential energy surfaces using XMS-CASPT2D.[3]

This research addresses the challenges of obtaining a reaction mechanism scheme from TRIR data, such as identifying intermediate structures, separating overlapping peaks, and constructing kinetically and thermodynamically logical schemes. Additionally, the study connects equilibrium experiments with TRIR experiments and employs computational chemistry to assign structures to intermediates, simulates reaction kinetics using rate constants and absorption coefficients.

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(P-21)

Single-Photon Transient Stimulated Emission Spectroscopy

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Recent progress in single-photon femtosecond spectroscopy has highlighted the crucial role of entangled photons in exploring material properties beyond the reach of traditional semiclassical approaches. In this work, we introduce a theoretically proposed technique named single-photon transient stimulated emission (SP-TSE), a new method in femtosecond time-resolved spectroscopy [1]. SP-TSE uniquely enables the selective probing of single-excitation superposition states and utilizes the quantum mechanical characteristics of photons for the efficient acquisition of transient response data, enhancing the practicality of SP-TSE experiments. A fundamental feature of SP-TSE is its employment of coincidence counting techniques to selectively detect two-photon states produced by stimulated emission. Our theoretical framework, bolstered by numerical simulations, demonstrates its effectiveness in elucidating the pure decoherence dynamics of a model molecular cavity system, thereby revealing quantum mechanical properties that are otherwise challenging to observe using conventional femtosecond time-resolved experiments.

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(P-22)

Simple preparation of photocatalytic titanium anode for efficient photoelectrocatalytic water splitting

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Facilitating water oxidation reaction (oxygen evolution reaction, OER) is crucial for achieving efficient hydrogen production through water splitting due to its inherently sluggish nature which requires high overpotential. The use of photocatalytic semiconducting materials as a photoanode has been considered as a promising approach to catalyze OER. Various metal-oxides based photoanodes have been synthesized and their photo-electro-catalytic activities towards OER have been studied.

In this work, we demonstrated that Ti-oxide based photoanode for photo-electro-catalytic water splitting can be prepared via a simple surface etching and post-annealing process. The photoanode was prepared by immersing the Ti foil into a hydrofluoric acid solution, followed by a thermal annealing under the ambient condition. The surfaces of Ti-oxide photoanode were carefully analyzed after immersion of hydrofluoric acid solution, thermal annealing at various temperatures (400, 600, and 800 °C) by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM). Additionally, their surface charge transfer behaviors were investigated by means of electrochemical impedance spectroscopy (EIS).

The results revealed that the nano-sized surface structures were formed on the surface Ti foil by exposure to hydrofluoric acid solution. The native amorphous Ti-oxide layers existed already on the surface of Ti foil was removed by hydrofluoric acid exposure, but the Ti-oxide layers were grown during the post-annealing process. As the annealing temperature increased, thicker Ti-oxide layers were formed, accompanied by the gradual sintering of small nanostructures on its surface. The sample annealed at 600 °C exhibited the highest efficiency towards water splitting reactions for hydrogen production under UV light and solar irradiation conditions (Air Mass 1.5); 1 x 1 cm^2 size sample produced 37.3 μmol hydrogen gases per hour, achieving 85% Faradaic efficiency for hydrogen production under 365 nm-light irradiations. This high efficiency can be attributed to high charge-transfer efficiency at the Ti-oxide anode/water interface, which seemed to be closely related to high surface roughness and coexistence of rutile and amorphous Ti-oxide phases. Scale-up experiments were also performed and the results proved that size of Ti-oxide photoanode can be easily scaled up while maintaining its photoelectrocatalytic activity towards water splitting reactions due to the simplicity of the preparation methods.

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(P-23)

Thickness-Dependent Excitonic Behaviors of 2D Tetracene Crystals at Various Temperature

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Recent studies on two-dimensional molecular crystals (2DMCs) revealed their unique physical, electrical, chemical, and optical properties distinct from their bulk counterparts. Molecular crystals are expected not only to manifest such size effects like the conventional inorganic 2D systems, but also enable diverse future applications. In this work, we exploited top-down mechanical exfoliation to form 2D tetracene (Tc) crystals and investigated their geometric and electronic structures using scanning probe microscopy and variable-temperature photoluminescence spectroscopy, respectively. Significant variations in absorption and emission spectra were induced as a function of temperature and thickness. The origins of the spectral changes will be explained in terms of phase transitions, trap states and electron-phonon couplings. We will also discuss the fate of molecular excitons confined in the 2D systems based on time-resolved photoluminescence measurements. The unique photophysical properties of two-dimensional Tc revealed in this work will lead to a deeper understanding of excitonic behaviors in low-dimensional molecular solids.

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(P-24)

Epi and Forward-Scattering Stimulated Raman Spectroscopy of 2D Inorganic and Organic Crystals

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Stimulated Raman spectroscopy (SRS), a coherent Raman scattering technique, offers significant benefits such as label-free imaging and signal amplification. These benefits not only overcome labeling-induced artifacts but also address the challenge of the inherently small Raman scattering cross-sections. Leveraging these advantages, SRS emerges as a potent tool for the characterization of two-dimensional (2D) materials with low Raman cross sections. In this work, we explored the limits of sensitivity in both epi and forward-scattering geometries using 2D hexagonal boron nitride (hBN) as an SRS reference. To mitigate instrumental noise, we implemented in-line balanced detection for both geometries. We also present the first demonstration of SRS spectral acquisition and imaging of 2D molecular crystals, specifically using mechanically exfoliated 2D pentacene. This study paves the way for broadening the applicability of SRS across a diverse array of 2D materials.

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(P-25)

Molecular Photothermal Effect on 2D-IR Spectroscopy in Acetonitrile-based Li-ion Battery Electrolytes: Insights from Cross-Peak Analysis

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Advances in lithium-ion battery (LIB) technology rely on a detailed understanding of charge transport mechanisms. Ultrafast two-dimensional infrared (2D-IR) spectroscopy has been widely used to investigate the dynamics of Li-ions in electrolytes due to its potential to directly probe exchange processes via time-dependent cross-peak analysis. However, the accurate interpretation of these dynamics is often complicated by factors such as vibrational energy transfer (VET) and the molecular photothermal effect (MPTE), both of which can influence the evolution of cross-peaks in 2D-IR spectra. The challenge of pinpointing the precise origin of these cross-peaks represents a significant hurdle in the study of LIB electrolytes. In this study, we closely track the origin of cross-peaks in 2D-IR spectra, focusing on C≡N vibrational modes within acetonitrile-based LIB electrolytes. Time-dependent 2D-IR cross-peak analysis of the -SCN mixture in CD3CN revealed distinctive features indicative of MPTE, a factor that cannot be overlooked in the study of LIB electrolyte dynamics. Furthermore, the direct observation of intermolecular MPTE through two-color IR pump-probe spectroscopy lends additional support to our findings. Our results underscore the non-negligible MPTE-induced artifacts in time-resolved IR spectroscopy and highlight the need for careful consideration of these effects to ensure precise observations of ultrafast dynamics within LIB electrolytes.

So Yeon earned her Ph.D. from Korea University in August 2023 and is currently pursuing a post-doctoral position at the same institution. Her research interests focus on exploring the use of time-resolved vibrational spectroscopy such as operando Raman, IR-PP, and 2D-IR spectroscopy in analytical applications.

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(P-26)

Visible transient absorption spectrometer with interferometry

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Visible transient absorption spectroscopy is a useful tool for investigating charge carrier dynamics. However, visible transient absorption requires single shot measurement for accurate data, which limits the use of slow CCDs. Here, we demonstrate a new detection scheme by combining the supercontinnum generation and interferometry. The interference pattern can be detected by commercial silicon photodiode, which do not need expensive fast CCDs. By using this method, we have confirmed the fundamental 800nm vs. 800nm interferometry is possible with our setup. The Fourier transform showed 800nm spectrum with 50nm FWHM, as seen by spectrometer. Currently, making a stable supercontinuum and making interference pattern with supercontinuum light is underway.

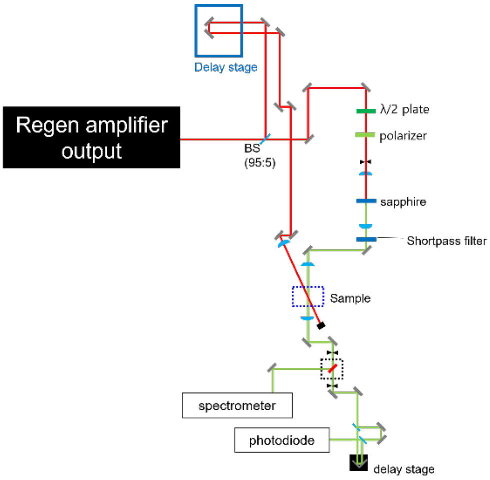

Fig. 1 Visible transient absorption spectrometer design with Mach-Zender interferometer

(P-27)

Functionalized 2D MXene coordinated with metal nanoparticles via microwave for electrochemical hydrogen fuel generation

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Two-dimensional (2D) transition-metal carbides (MXenes) are widely used as promising electrocatalysts/support in electrochemical reactions due to their excellent metallic conductivity and large surface area. In this study, we explore the enhancement of hydrogen evolution reaction (HER) efficiency by coordinating metal nanoparticles to functionalized MXene using a rapid microwave strategy. MXene was functionalized with organic ligands to improve its interaction with metal nanoparticles and prevent surface oxidation. The metal nanoparticles were then uniformly distributed on the ligand-modified MXene surface through microwave irradiation, forming a robust conductive network that maximized electron transfer efficiency. The performance of the MXene-metal nanoparticle composite as a catalyst for the hydrogen evolution reaction was evaluated, demonstrating a significant improvement compared to unmodified MXene. This research introduces a novel approach to developing high-performance HER catalysts, suggesting substantial potential for improving the efficiency of hydrogen fuel generation.

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(P-28)

Utilizing Liquid Phase Pulsed Laser for Valuable Material Recovery from Waste Solar Panels

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The solar power industry has developed rapidly to realize carbon neutrality, and it is expected that at least 1.7 million tons of waste crystalline silicon (c-Si) photovoltaic (PV) modules will be released from 2030. Silver and silicon, crucial components of these modules, pose significant recycling hurdles due to complex processes and high costs. Using a pulsed laser, high-purity silver and silicon were successfully extracted from leachate derived from waste c-Si PV modules. The process involved irradiating the leachate with a nanopulse laser at specific parameters. Recovery rates varied based on impurity removal. Characterization of the recovered silver and silicon particles was conducted using SEM/EDS, XRD, and ICP-OES techniques. The recovered materials show promise for applications in cutting-edge semiconductor technology, contributing to sustainable practices in the solar energy industry.

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(P-29)

Enhancing the electrochemical behavior of Nickel Cobalt Oxalate/MXene Composites based supercapacitors with Aqueous Electrolytes/Ionic Additives

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Nickel cobalt oxalate ($NiCoO_x$) has garnered significant attention as an electrode material for supercapacitors due to its better morphological and electrochemical properties. However, its performance is often hindered by low conductivity and limited ion accessibility. In the present study, we report a new strategy to enhance the electrochemical properties of $NiCoO_x$ by incorporating MXene, a two-dimensional transition metal carbide, as a conductive additive. The synthesis of $NiCoO_x$/MXene composite was carried out by a low-temperature KOH-assisted method. Structural and morphological analyses confirmed the successful integration of MXene into the $NiCoO_x$ matrix, resulting in increased surface area, porosity, and conductivity. The procured electrochemical properties revealed that the composite electrode exhibited significantly higher specific capacitances compared to traditional $NiCoO_x$-based materials. Moreover. In this work, key performance factors such as electrolyte concentration, KOH concentration, and operating voltage were systematically investigated. Higher concentrations of $K_4Fe(CN)_6$ enhanced the pseudo-capacitance properties, while an optimal KOH concentration facilitated double-layer capacitance. The operating voltage significantly influenced the extent of redox reactions and the contribution of pseudo-capacitance. Overall, the $NiCoO_x$/MXene composite, synthesized via a simple KOH-assisted method, presents a promising approach for the development of high-performance supercapacitors with enhanced electrochemical properties.

Keywords: Nickel cobalt oxalate, MXene, Specific capacitance, Pseudo-capacitance, Double-layer capacitance, Operating Voltage

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(P-30)

Enhancing the Stability of High-Energy Lithium-Ion Batteries with MXene/Carbon Nitride Hybrid Materials

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In the face of growing energy demands, lithium-sulfur (Li-S) batteries have emerged as a promising solution, boasting a remarkable six-fold increase in capacity over conventional lithium-ion batteries. However, they grapple with challenges such as the shuttle effect. To address this, the sulfur and carbon (S/C) composite is prepared by melt-mixing method. The C_xN_y phase was synthesized hydrothermally and confirmed using X-ray diffraction (XRD) analysis. The optical absorption spectra of the synthesized C_xN_y sample revealed the formation of C_xN_y with a strong absorption at the visible region. The C_xN_y and MXene composite was utilized to solve the shuttle effect and improve the electronic conductivity. Through extensive electrochemical analyses including cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge-discharge studies, using a 1 M LiTFSI in DME:DOL electrolyte, significant improvements were observed in battery performance as well as cycling stability. These findings offer crucial insights for the advancement in battery performance and energy storage applications.

Keywords: C_xN_y, MXene, Lithium-sulfur battery, Shuttle effect, Energy storage

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(P-31)

Enhanced Electrochemical Behavior of LASER-Synthesized $BaTiO_3$/MXene Composite

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The integration of advanced 2D-layered materials in supercapacitor design has garnered significant attention due to their potential to meet the growing demand for high-performance energy storage applications. In the present study, we report the LASER-assisted synthesis of $BaTiO_3$/MXene nanocomposites for high-performance supercapacitor applications. Incorporation of MXene into the $BaTiO_3$ framework has significantly enhanced specific capacity and long-term stability. Structural and morphological analyses revealed the particle sizes ranging from 80 to 100 nm, indicating the successful synthesis of the nanocomposite materials. Galvanostatic charge-discharge (GCD) analysis further demonstrated the superior performance of the $BaTiO_3$/MXene supercapacitors, showing enhanced specific capacity values when compared with corresponding counterparts. Finally, the obtained higher performances and long cycle life properties of $BaTiO_3$/MXene composite demonstrated that it could be a promising candidate for high-performance energy storage applications.

Keywords: Barium titanate, Supercapacitor, Stability, MXene, Electrochemical analysis, LASER synthesis

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(P-32)

Exploring anion exchange in highly luminescent lead free halide perovskites ($CsCuX_3$, X= Br, Cl)

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The novelty of lead-free cesium halide perovskite nanocrystals, which share a crystal structure compatible with existing cesium lead halides, has garnered significant interest. Post-synthesis chemical transformations of colloidal nanocrystals, specifically focusing on anion-exchange reactions in lead-free cesium halide perovskite nanocrystals. In the current work we report a new approach of tunable anion exchange in $CsCuBr_3$ nanocrystals to form $CsCuCl_3$ perovskite. The extent of anion exchange is monitored through shifts in fluorescence emission peaks and ultraviolet-visible absorbance edges, controlled by adjusting the absorbed doses. The study reports fast, room-temperature, and deliberately partial or complete anion-exchange in luminescent semiconductor nanocrystals of lead-free cesium halide perovskites ($CsCuX_3$, X = Cl, Br). By tuning the halide ratios, the photoluminescence can be observed across the blueish -green part of visible spectral region (410–510 nm), while maintaining high luminescence and broad emission. With high quantum, yield of about 92 %.

Keywords: Lead free halide perovskites, cesium halides, quantum yield, luminescence, anion exchange

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(P-33)

Electrochemical Insights of MXene-La_2CoNiO_6 Composites for enhanced Supercapacitive Performance

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In the present study, we report the successful synthesis of MXene/La_2CoNiO_6 double perovskite composites for supercapacitor applications. MXenes, known for their exceptional electrical conductivity and substantial surface area, were synthesized in tandem with KOH-assisted La_2CoNiO_6 double perovskite nanoparticles using wet chemical method. The composite materials were produced through a simple process of mixing and subsequent annealing. Structural characterization using X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the formation of the composites, revealing a well-defined structure and intimate interfacial contact between MXene and La_2CoNiO_6. Electrochemical evaluations demonstrated that the MXene/La_2CoNiO_6 composites exhibit superior capacitance and cycling stability compared to their individual components, attributed to the synergistic effects arising from the combination of MXene high conductivity and La_2CoNiO_6 pseudocapacitive properties. The enhanced electrochemical performance of these composites is due to the effective integration of MXene and La_2CoNiO_6, which facilitates rapid electron and ion transport, thereby improving charge storage and stability. The promising electrochemical properties of the MXene/La_2CoNiO_6 composites, characterized by high specific capacitance, excellent rate capability, and robust cycling stability, underscore their potential as high-performance materials for advanced supercapacitor applications. In conclusion, the MXene/La_2CoNiO_6 double perovskite composites represent a significant advancement in the field of supercapacitors, providing a novel approach to achieve high energy and power density, essential for various energy storage applications.

Keywords: MXene, La_2CoNiO_6, double perovskite, supercapacitor, wet chemical synthesis electrochemical performance, specific capacitance, cycling stability

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(P-34)

Binder-free Copper Nickel-based Nano Architectures on MXene Sheets Enfolded Carbon Cloth as a Multifunctional Material for Energy Conversion and Storage Applications

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Investigating cost-effective and high-performance electroactive materials for energy conversion and storage application is crucial to effectively address the looming energy crisis. Herein, we report the binder-free copper nickel-based nano-architectured material on 2D MXene sheets enfolded carbon cloth (MXene-CuNi/CC) using a facile hydrothermal technique. The effects of the morphological, elemental, and surface area properties of the synthesized binder-free electrode materials on their electrochemical properties were distinctly studied. The optimized MXene-CuNi/CC electrode exhibited superior specific capacity values when compared with the other electrode materials and revealed excellent cycling stability properties. Moreover, the optimized MXene-CuNi/CC electrode exhibited excellent bifunctional electrocatalytic results with lower overpotential values. Furthermore, the assembled flexible hybrid supercapacitor (HSC) device revealed desirable electrochemical performances, superior energy and power density values, and long cycling stability properties. These procured superior results suggested that MXene-CuNi/CC is one of the most effective electroactive materials for energy conversion and storage applications.

Keywords: MXene, Copper-nickel nano architectures, Binder-free electrodes, Hybrid supercapacitors

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(P-35)

Lipid-modified DNA self-assembly and interaction with bilayer membrane using coarse-grained molecular dynamics

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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, formingspherical micelles with a hydrophobic core and DNA corona in an aqueous phase. In addition, U4Ts enhance cell permeability through the interactionbetween the uracil bases and the lipid bilayer of a cell membrane. In this research, the aggregation of U4Ts and the U4T-bilayer interaction were studied bymolecular dynamics simulations. We investigated the self-assembly behavior of U4Ts within a specified time and determined the aggregation number of U4Tmicelles by coarse-grained (CG) simulations. Furthermore, we observed the interactions of U4Ts and dipalmitoylphosphatidylcholine bilayer by all-atom (AA)and CG simulations. We found that U4Ts can aggregate into spherical micelles with excellent stability and are capable of docking onto cell membranes.

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(P-36)

Thermodynamic principles governing nucleus seed formation and phase separation

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Supersaturation and nucleus seed formation precede all phase transitions, yet the underlying thermodynamic principles remain incompletely understood. We here introduce new thermodynamic formulas governing the supersaturation degree, the size distribution and free energy of nucleus seeds, and their phase transition. These exact results show that, under supersaturation, the largest cluster size (LCS) is an important state-variable; the supersaturation degree decreases with the LCS, approaching unity in the macroscopic limit. The size-distribution of nucleus seeds is either a unimodal or a monotonically decreasing function of size, depending on the system, environment, and temperature. We discover and identify the critical supersaturation degree, at which the seeds undergo the phase transition during which the most probable size exhibits an abrupt increase. We also investigated nonequilibrium dynamics of supersaturation, nucleus seed formation, and ensuing phase transition, accounting for the monomer-supply-rate effects. Nucleus seeds attain either nonequilibrium-steady-state (NESS) or transient-oscillatory-state (TOS) depending on the monomer-supply-rate, before undergoing the phase transition. In both NESS and TOS, nuclei assume a quasi-equilibrium size distribution; their population exhibits a universal power-law relaxation during the phase transition. This work can be extended to investigate diverse nucleation and phase transition phenomena prevalent across nature and industry.

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Comprehensive analysis of fluorescent protein expression in response to external signals

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Fluorescent proteins are effective tools for quantifying gene expression dynamics in living cells. While it is known that these proteins emit fluorescence upon undergoing maturation processes, the impact of these processes on protein levels measurable by fluorescent proteins remains unclear. Here, we propose a new version of the chemical fluctuation theorem (CFT) that applies to fluorescent proteins expressed in a burst manner and can be used to analyze experimental observables such as the mean and variance of matured protein levels in living cells. We also explore intracellular response dynamics triggered by external stimuli such as transcriptional induction or antibiotic stress. This research provides a reliable and quantitative tool to analyze time-dependent cellular response to various signals.

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(P-38)

Quantum Chemical Studies on the Photochemical Behavior of Benzene Derivatives through the Antiaromatic Reaction Coordinate

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With the development of computational tools and analysis methods, various kinds of theoretical investigations on benzene has been gaining reignited interest. Based on the Baird's rule, the S_1 state of benzene is known as anti-aromatic, and numerous studies attribute its reactivity to this antiaromatic nature. However, considering the photochemistry of another benzene derivatives with heteroatoms or additional functional groups, arguing the origin of reaction with only antiaromaticity is not proper to explain the whole scenario. To elucidate the nature of photochemical bond rearrangement in the S_1 state of benzene-like compounds, we conducted molecular orbital-based analyses on the excited states of these compounds, including those with heteroatomic substitutions, using state-averaged CASSCF calculations. Our analyses reveal that the major excitation characters of the S_1 state play a crucial role in the excited state reaction involving ring puckering coordinates, and substituents significantly impact the frontier molecular orbital energies, so that the resulting PES energy can be tuned by heteroatomic substitutions. Nonadiabatic molecular dynamics simulations on such systems show an impact of the energy changes on S_1 state in quantitative manner, such as the decay ratio of S_1 state and the ratio of photoisomerization after the S_1/S_0 state crossing. Collectively, the molecular orbital analyses and nonadiabatic molecular dynamics simulations unveil the intricate interplay between the antiaromatic nature of the S_1 state, excitation characters, and substituent effects in governing the photochemical reactivity of benzene-like compounds, paving the way for a deeper understanding and potential applications.

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Deep Learning Strategy for Prediction of Physical Properties in Multicomponent System

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Precise prediction of physiochemical properties in multicomponent system, such as solution, has industrial and scientific importance yet presents significant challenges, requiring advanced computational strategies that account for complex molecular interactions and compositional variability. While deep learning method and other computational method have been widely used for predicting molecular properties, mostly for single molecules, such methods have used simple molecular representations that often fail to capture intra-molecular interactions and overlook the compositional effect. This study introduces a comprehensive graph-based deep learning framework designed to enhance prediction accuracy in multicomponent systems by considering the environment of each component molecules. The distinctive feature of the model is the development of environmental feature, which are in situ embeddings generated during training to dynamically represent the environmental factors influencing molecular characteristics. This approach can accurately learn the interaction between the molecules under mixture system condition, thereby significantly enhancing tis predictive accuracy for physiochemical property, flash point in this study. Trained on an extensive dataset of both experimental and computational data, our model outperforms existing methods in accuracy and computational efficiency, paving the way for advanced deep learning applications in complex chemical systems and offering a powerful tool for scientific and industrial applications.

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Greenhouse gases metrology based on photolysis laser-induced fluorescence (LIF) spectroscopy

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The determination of atmospheric lifetimes for greenhouse gases constitutes a crucial element in comprehending their impact on global warming. Therefore, global warming potential (GWP) is developed. The GWP is described by radiative forcing and atmospheric lifetime. Nevertheless, there needs to be more available data related to atmospheric lifetimes. To address this disparity, we have adopted a homebuilt laser-induced fluorescence (LIF) system. This LIF setup comprises four components: the gas inlet, the gas pumping, the laser unit, and the data acquisition systems. Our LIF setup is meticulously designed to maintain gas pressure at a constant level, ensuring precise measurements of atmospheric lifetimes In our research, we have obtained LIF signals for two key substances: OH radical and 1,1,1-trichloroethane (CH_3CCl_3, TCE). Importantly, our findings are rigorously validated through comparisons with previous research. Moreover, our instrument is verified by traceability from KRISS. As a result, our study contributes to the measurement of atmospheric lifetimes to the accuracy and dependability. Furthermore, we provide a quantified measure of uncertainty, enhancing the precision and reliability of these vital values. This advancement in understanding atmospheric lifetimes is a significant step for measuring GWP.

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(P-41)

Polarized Absorption Spectroscopy of 2D PTCDA Crystals Grown on Graphene and Hexagonal BN

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The fate of excitons in a semiconductor is governed by its band gap and their binding energy, which are influenced by the dielectric screening. Excitons in two-dimensional (2D) systems are more strongly bound for reduced screening and can be tuned by engineering the effective dielectric constant [1,2]. In this work, we investigate how the reduced dielectric screening affects molecular excitons residing in 2D molecular monolayer and explore the possibility of their Coulomb tailoring. Using physical vapor assembly, we prepared 2D crystals of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) on top of several-layer hexagonal BN and graphene [3]. The excitonic absorptions obtained by angle-resolved differential reflectance spectroscopy revealed Davydov splitting in Frenkel-type S_0-S_1 vibronic transitions for 1L PTCDA without charge transfer mixing. The presence of graphene induced substantial spectral changes in Frenkel excitons: red-shift, broadening and reduced Davydov splitting. We will discuss their mechanistic origins and future investigation using variable-temperature and polarization-resolved methods.

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(P-42)

Phase separation of ternary lipid mixtures dependent on the curvature of liposomal membrane: in silico approach

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Although phase behaviors in planar membranes are well characterized[1], those in highly curved liposomes have not been less understood[2]. Here, we investigated the curvature dependence on the preferential positioning of lipid domains in phase-separating liposomes. We consider ternary lipid mixtures composed of saturated lipids, unsaturated lipids, and cholesterols, with a composition of DPPC:DIPC:CHOL = 50:30:20, where DPPC, DIPC, and CHOL refer to dipalmitoyl phosphatidylcholine, dilineoyl phosphatidylcholine, and cholesterol, respectively. All simulations were performed using coarse-grained Molecular Dynamics (MD) simulations with the MARTINI 2.0 force field. To investigate the curvature dependence, we applied uniaxial compression to the liposome along the z direction, inducing the deformation to flat pancake-shaped structures with three fixed heights of 12, 16, and 20 nanometers. The results show that DPPC/CHOL-abundant and DIPC-abundant phases separate between flat surfaces and curved edges depending on the edge curvature within uniaxially compressed liposomes. For vesicles compressed to 20 nanometer, neither DPPC/CHOL nor DIPC domains showed a distinct preference for the curved edges. However, at a height of 16 nanometer, DPPC/CHOL domains were preferentially located at the curved edges, whereas at a height of 12 nanometer, DIPC domains were mainly found at the curved edges. This work suggests that the patterns of phase-separating liposomes can be controlled by applying uniaxial compression.

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(P-43)

Integrated method for identifying the optimal descriptor of acute critical illness: Development of septic infection related risk index (SIRRI) and investigation into patient's fate dynamics along SIRRI

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Acute critical illnesses, particularly sepsis, pose significant challenges due to their sudden life-threatening nature and heterogeneous pathologies, demanding early detection and appropriate treatment [1]. The lack of golden standards for early sepsis diagnosis has led to the exploration of deep learning (DL) methods for diagnostic or prognostic purposes, despite their opaque decision-making processes [2]. Here, we propose a systematic and transparent method that integrates a DL module for early sepsis diagnosis, an explanation module for assessing feature importance and selecting key features, and a module for constructing multidimensional spaces defined by features generated through the application of mathematical operators to the identified features. Using this integrated method, we establish a septic infection-related risk index (SIRRI), composed only of six infection or inflammation-related biomarkers, as the optimal descriptor characterizing the severity of pathology in sepsis patients. In addition, we develop a prognosis model based on a set of multi-stage reaction-diffusion equations in SIRRI coordinates, enabling the prediction of time-dependent mortality or recovery rates of sepsis patients based on their SIRRI values at the onset of sepsis, with applicability across multiple datasets. These results demonstrate the utility of SIRRI as a novel effective biomarker for both diagnosis and prognosis in clinical practice, with potential applications extending beyond sepsis to other acute critical illnesses.

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(P-44)

A Theoretical Study on the Reactivity and Mechanism of Mn(V) Hydroxo Porphyrin in Hydroxylation Reactions , A Deep Dive into its Catalytic Magic

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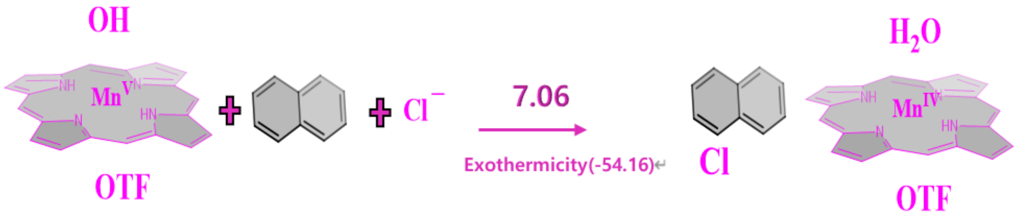
Aromatic halogenation reactions play a crucial role in various fields, including pharmaceuticals, materials science, and agrochemicals. The use of Mn(V) hydroxo porphyrin complexes as catalysts for aromatic halogenation is a promising and versatile approach. However, understanding the underlying mechanisms 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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Bioinformatic Analysis of Protein Structures Using Contact Map Formalism

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Structural information of a protein is the key to understanding its function. Various experimental approaches have been developed to determine protein structures, leading to the construction of a database that contains hundreds of thousands of protein structures. The extensive database can be used to uncover the principles governing protein folding and design. Previous studies indicate that the topological information of protein structures is often sufficient to extract these fundamental principles. One representation of protein topology is a contact map (CM), which is a 2-dimensional matrix that contains information about the non-covalent contacts between residues in a protein. In this study, we tested several quantities (such as trace and element sum) derived from a CM to characterize protein structures, and we found that CMs and their derived quantities can reveal the structural and evolutionary diversity of proteins. We anticipate that these measures, based on CM, have the potential to serve as a straightforward and effective proxy for evaluating the evolvability of proteins. Furthermore, they can play a crucial role in facilitating the de novo design and engineering of biomolecus.

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Simulation Study on the Frequency Dependent Mechanical Properties of Semi-crystalline Block Copolymers

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Dynamical Mechanical Analysis (DMA) is a widely used experimental technique to investigate the viscoelastic properties of polymer materials. This method involves applying a sinusoidal strain on samples and measuring the mechanical response (stress, moduli, phase shift, etc.). DMA results are crucial for understanding the mechanical strength of polymers across a wide range of frequencies and temperatures via time-temperature superposition (TTS).

Also, DMA has been widely used for thermoplastic elastomers (TPEs) to investigate their service temperature ranges, mechanical hardness, and viscoelastic energy dissipation. TPEs are block copolymers composed of crystallizable hard and amorphous soft blocks, which form microphase-separated domains. Clearly, the molecular motions within these domains would be activated at different temperatures and timescales. Therefore, it is essential to understand how these crystalline and soft domains influence the frequency-dependent mechanical properties of TPEs across varying temperatures.

We investigate the frequency-dependent mechanical properties of TPEs using a modified Kremer-Grest model. Studies have shown that, compared to the Green-Kubo method, non-equilibrium molecular dynamics (NEMD) method provide better agreement with experimental DMA data.[1,2] Therefore, we conduct NEMD simulations that mimic DMA experiments. The model involves two types of beads: hard (crystallizable) and soft (amorphous). The detailed simulation procedure includes: 1) Equilibration (T=4), 2) Cooling below the T_C of the hard segments, and 3) DMA simulations. We evaluate the applicability of NEMD on this coarse-grained TPE model and find that the storage and loss moduli are quantitatively obtainable above the T_C of the hard segments. Consistent with experimental observations, we identify non-linear trends of tan δ as a function of frequency. Furthermore, we present the molecular motions within the crystalline and soft domains during DMA under different temperatures and frequencies, providing insights into the dynamic behavior of TPEs.

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(P-47)

Chemomile: Geometry-based Explainable GNN Model for Predicting Combustion Properties

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Prediction of combustion-related properties, such as flash point (FP), autoignition temperature (AIT), the heat of combustion ($\mathit{\Delta H}_{\mathrm{comb}}$), and upper/lower flammability limits (UFL/LFL), are crucial in the industry since inaccurate prediction may lead to serious safety concerns. While accurate prediction is needed, it remains challenging because most combustion reactions occur under high temperature and pressure. Though many models based on graph neural networks (GNN) have been introduced to minimize errors, most of them undermine the hierarchical aspect of a chemical compound. Here, we introduce Chemomile, designed to incorporate the 3D geometry of atoms and collective influences of groups of atoms in a molecule. The model uses two-level graph representation; intra- and inter-fragment level. Chemomile first divides a molecule into fragments and each fragment can be converted into a graph of the intra-fragmental structure of atoms and bonds. Similarly, the inter-fragmental graph depicts the connectivity between fragments. At each level, the graph attention network summarizes the structural information into embeddings, which are later utilized to predict a property. Particle swarm optimization (PSO) was chosen for hyperparameter optimization due to its suitability for parallelization compared to iterative techniques like Bayesian optimization (BO). The benchmark result of the optimized model with the estimated solubility database (ESOL) shows comparable performance to recent ones. The model is also tested on combustion-related properties, and the contribution of each fragment can be analyzed using a perturbation-based explanation algorithm, which can provide chemists with new insights into structure-property relationships.

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Multiphasic growth dynamics of nanoparticle ensembles: Genetic algorithm-based quantitative analysis

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Colloidal nanoparticles are of great interest in modern science and industry. However, thermodynamic origin and temporal dynamics of the nanoparticle growth remain elusive. Addressing these issues, we tracked hundreds of growth trajectories of a nanoparticle ensemble using liquid-phase-TEM. Through this investigation, we discovered that nanoparticle growth exhibits size-dependent multiphasic dynamics which is inconsistent with current theoretical frameworks. Inspired by this discovery, we developed a non-classical theory for growing nanoparticles. This theory provides a quantitative understanding of the time-dependent mean and fluctuation of nanoparticle size, as well as size-dependent growth rate profiles for various nanoparticle systems and experimental conditions. Our work demonstrates the power of the quantitative approach by extracting microscopic parameters characterizing physicochemical properties of nanoparticle systems using genetic algorithm. Moreover, we found out that the chemical potential in a nanoparticle significantly deviates from the classical nucleation theory and uncovered how it governs size-dependent growth dynamics of nanoparticles, in conjunction with the time-dependent monomer concentration.

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Elucidation of Equilibrium Size Distribution of Rigid Clusters and Bio-Condensates

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Supersaturation and nucleus seed formation are universal processes that precede all phase transitions. Despite extensive research on nucleation, our understanding on supersaturation, and nucleus seed formation remains rudimentary. In this poster, we present the exact statistical thermodynamic formula for the saturation degree, the most-probable size distribution of mesoscopic nuclei, and their phase transition, introducing the mesoscopic state defined by temperature, the total monomer concentration, and the largest cluster size (LCS). These results show that supersaturation emerges even at equilibrium for mesoscopic nuclei systems and decreases with the LCS. The size-distribution of nucleus seeds is either a unimodal or a monotonically decreasing function of size, depending on the system and temperature. There exists a critical supersaturation condition under which nucleus seeds undergo a phase transition, during which the most probable size exhibits an abrupt change. In addition, we found that our non-classical nucleation theory fit well in real systems; Gold Nanoparticle, FePt Nanoparticle, InP Quantum dot, PRM-SH3-6His aggregate, mutant p53 aggregate [1], and IDP-2Yx2A micelle [2]. This work can be extended to investigate diverse nucleation and phase transition phenomena prevalent across nature and industry.

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(P-50)

Mechanism of [1,5]-Brook Arrangement of 3-Amidobenzyne precursor

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For the formation of a benzyne precursor, two mechanistic pathways are proposed: (1) C-to-O [1,5]-Brook rearrangement and (2) C-to-N [1,3]-aza-Brook rearrangement. Using DFT calculations in a polar solvent, we found the [1,5]-shift to proceed through a six-membered transition state with an activation energy of 27.72 kcal/mol, while the [1,3]-shift forms a four-membered transition state with an activation energy of 34.40 kcal/mol. The IRC profile shows that the [1,5]-shift has a shallow minimum, while the [1,3]-shift has a flat energy region near the transition state. The [1,5]-Brook rearrangement is kinetically more favorable due to less ring strain and higher interaction stabilization energy. Piperidine addition after the [1,5]-shift occurs at the meta position, consistent with experimental data. These findings provide insights into amidobenzyne formation, useful for reaction engineering and synthetic development.

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(P-51)

Machine-Learning Approach in Prediction of the Wettability of a Surface Textured with Microscale Pillars

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Tuning the wettability of a flat surface by introducing an array of microscale pillars finds wide applications, especially in engineering a superhydrophobic surface. [1,2] The wettability of such a pillared surface is quantified by the contact angle (CA) of a water droplet.[3] It is desired to know the CA prior to construction of pillars, in order to obviate the trial-and-errors in experimenting with many different topographies.

Given an accurate theoretical prediction of CA, typically Wenzel (WZ) and Cassie-Baxter (CB) model [4,5], has been elusive, we propose a convolutional neural network (CNN) model of CA for a surface patterned with rectangular or cylindrical pillars. By employing a three-dimensional descriptor of the surface topography, the present CNN model can predict experimental CA within errors comparable to the uncertainties in measuring CAs.

Our results demonstrate that the CNN model not only enhances the efficiency of designing superhydrophobic surfaces but also provide a reliable alternative to experimental methods. By minimizing the need for extensive empirical testing, this model paves the way for more cost-effective development of advanced surface engineering.

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Molecular Dynamics Simulation on the Growth of Methane Hydrate in the Presence of Amylose

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Gas hydrates are ice-like nonstoichiometric crystalline compounds in which gas molecules are wrapped in water molecules under high pressure and low temperature conditions. The growth of gas hydrate in gas pipelines can cause serious problems in the industry, by blocking the flow of oil and gas. Thermal hydrate inhibitors (THIs), or kinetic hydrate inhibitors (KHIs) are frequently used method to prevent the formation of hydrate. In this study, we investigated kinetic inhibition effect of amylose by using all-atom molecular dynamics (MD) simulation. Snapshots of the system over time, the total number of hydrate cages, and the potential energy of the system were used to investigate the effect of amylose on hydrate growth. hydrate growth rate was slower when amylose was present on the hydrate surface compared to when it was not.

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(P-53)

Preparation of Antimony-doped Tin Oxide Coated TiO_2 Micro-rods with Low Resistivity for the Application of Electric Painting Materials

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For the applications of TiO_2 micro-rods as electric painting materials, TiO_2 micro-rods were systematically investigated by synthesizing through ion exchange and controlled calcination methods. TiO_2 micro-rods have a length of 4-8 μm and a length-to-diameter ratio of 13-28. Compared with the other strategies previously used for the synthesis of TiO_2 rods, it was found that large-scale production was possible under mild reaction conditions, which can allow a facile and mild route for industrial application and can be expanded for the versatile applications of TiO_2 micro-rods.[1-2] Additionally, one-dimensional conductive TiO_2 micro-rods coated with antimony-doped tin oxide ($ATO@TiO_2$) were prepared using a hydrothermal coprecipitation method. Specially, cetyltrimethylammonium bromide (CTAB) surfactant was used as an interfacial adhesive and dispersing agent to form excellent and homogeneous active groups on the surface of TiO_2 rods. 0.2 g $ATO@TiO_2$ rods were compression-molded under a pressure of 2.0 ton for 3 min to form a disk with a diameter of 1.3 cm. And the $ATO@TiO_2$ micro-rods exhibited a resistivity as 70 ± 0.5 Ω measured by a resistivity meter (4-point probe).[3] The morphology and composition of ATO coated TiO_2 micro-rods were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

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(P-54)

Solar liquid fuel production by using Mo-doped $BiVO_4$ as photoanode and multilayered CuNi alloy/N-doped reduced graphene oxide/nafion as dark cathode

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The abatement of increased CO_2 levels in the atmosphere is of great concern to improve the climate quality.[1] On the other hand, the production of valuable chemicals from the renewable energy sources (solar and wind) is of paramount interest.[2] In this regard, the solar liquid fuel (such as methanol and ethanol) production from the photoelectrochemical (PEC) CO_2 reduction evolved as a sustainable and promising method.[3] However, the solar to fuel conversion is hugely dependent on the efficient photoanodes which can produce high currents upon light illumination, and the dark cathodes which can selectively produce the liquid products. In this work, we attempted to develop Mo-doped $BiVO_4$ photoanode and CuNi alloy/N-rGO/nafion dark cathode system to produce the methanol and ethanol selectively. The incorporation of Molybdenum (Mo-) into $BiVO_4$ is expected to increase the photocurrent density by increasing the absorption co-efficient and by decreasing the recombination rate of the charge carriers. Meanwhile, the individual component in the multilayer cathode has a specific role for selective product formation. The CuNi alloy can selectively produce an important 'CO' intermediate during the CO_2 reduction reaction, the N-doped reduced graphene oxide (N-rGO) is beneficial for the multielectron shuttling and CO_2 adsorption/ activation, and the nafion layer promotes the proton migration. With the aid of multi proton/electron shuttling, the produced 'CO' intermediate over the CuNi alloy will eventually produce the solar liquid products. The electrodes fabrication procedure and their physical characterization results will be presented during the conference.

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(P-55)

Degradation of Low-density Polyethylene (LDPE) into Gasoline and Diesel Fuels at Low Temperature Using Defectronics Based Amorphous Silica-alumina (ASA) Cayalyst

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Thermal degradation of waste plastic is a prospective way of converting waste plastic into low-emissive hydro-carbon fuel. The present research is focused on converting waste plastic into low-emissive hydrocarbon fuel by two processes: high-temperature thermal degradation without a catalyst and catalytic cracking under low-temperature. LDPE, which is the most commonly produced and difficult-to-decompose type of waste plastic, was used instead of converting it into gasoline. TGA was used to examine the effect of catalysts in the decomposition reaction and degradation temperature of LDPE. The thermal degradation takes place from 250 °C to 500 °C with and without a catalyst. When a catalyst was used, the decomposition reaction temperature was lowered to 200 – 250 ºC and the decomposition efficiency was much enhanced. Qualitative analysis of the decomposition products was performed through GC and GC-Mass analysis. Simulated distillation (SIMDIS) analysis results showed that when LDPE was decomposed using an ASA catalyst, approximately 70% gasoline and 20% diesel fuel were produced at 200 – 250 ºC.

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(P-56)

Preparation of colloidal ZnTe/g-C_3N_4 quantum dots based efficient photocathode for photoelectrochemical reduction of CO_2 into solar liquid fuels

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One of the most environmentally friendly ways to combat climate change is to employ renewable energy sources to cut carbon emissions. Photoelectrochemical CO_2 reduction offers promising ways for converting CO_2 into value-added fuels and chemicals using solar energy. The photoelectrochemical CO_2 conversion to C_2 products are more advantageous due to its greater energy density and higher commercial value over their C_1 counterparts. The present work is focused on the preparation of novel ZnTe/g-C_3N_4 quantum dots-based photocathode for better selectivity towards C_2 products. The ZnTe/g-C_3N_4 quantum dots-based photocathode exhibits significantly improved photoelectrochemical performance compared to pristine ZnTe and g-C_3N_4. The synergistic effect between ZnTe and g-C_3N_4 quantum dots facilitated efficient charge separation and transfer, leading to enhanced photoelectrochemical CO_2 reduction activity. The products derived from ZnTe-based photocathode are primarily to be the C_1 products (mainly CO) with severe competition of hydrogen evolution reaction. Therefore, it is necessary for ZnTe to design a heterojunction to improve charge separation and selectivity of C_2 products. The developed ZnTe/g-C_3N_4 quantum dots-based photocathode holds great promise for efficient and selective photoelectrochemical CO_2 reduction, offering a sustainable approach towards renewable fuel production and CO_2 mitigation.

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(P-57)

Efficient photocatalytic CO_2 reduction with single 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.

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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.

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DFT Calculations on the Reaction Pathway to Convert CO_2 to Formic Acid with High Selectivity using Ni-Perylene-Carbon Nitride Nanosheet (Ni-P-g-C_3N_4) Photocatalyst

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Photocatalytic CO_2 reduction reaction (CO_2RR) into value-added oxygenated products is one of the most promising ways of solving climate warming change and energy crisis simultaneously. To reach high selectivity and productivity of oxygenated fuel products, it remains great challenge in controlling both simultaneous sequential multi-electron/proton shuttling function through different transporting pathway, which determines the different intermediates and final products. To achieve this goal, we designed Ni-P-g-C_3N_4 catalyst for the highly selective production of formic acid (HCOOH) from photocatalytic CO_2RR.

As we know, CO_2 to HCOOH is two electrons and two protons transferred process. To identify this selective reduction mechanism from CO_2 to HCOOH, we carried out DFT calculations using Dmol^3 in Materials Studio 2023 software. The CO_2 adsorbed, intermediates and HCOOH adsorbed models, which can be obtained during the CO_2 photoreduction process, have been constructed and got the optimized structures and electronic properties. From the obtained structures, free-energy profiles, and free energy comparisons between reactant CO_2 and key intermediates together with molecular orbitals, we can identify the reaction pathway of CO_2RR. Ni ion tends to activate CO_2 molecules and intermediates through oxygen-bound mode which suppressed the CO production via carbon-bound mode. After CO_2 adsorption, the first proton was prone to be added firstly on the oxygen atom of $CO_2^{\bullet-}$ to form *COOH intermediate, rather than on the carbon atom of $CO_2^{\bullet-}$ to form *OC(H)O intermediate. Highly selective oxygenated formic acid was achieved through controlled reaction pathway of $*CO_2^{\bullet-} \rightarrow *COOH \rightarrow *COOH^- \rightarrow HCOOH$.

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(P-60)

Efficient Photocatalytic Reduction of CO_2 into Solar Liquid Fuels Utilizing Visible Light Active Cu Single Atoms Incorporated C-Doped K-Intercalated Poly(heptazine imide)

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The development of artificial photocatalytic CO_2 conversion into valuable fuels using sunlight is a promising approach to address climate change and achieve carbon neutrality. However, current photocatalysts often suffer from limitations such as low product selectivity towards C2+ hydrocarbons.[1] This study presents a novel strategy for synthesizing a highly efficient photocatalyst for CO_2 conversion to C2+ fuels. We report the successful synthesis of Cu single atoms incorporated C-doped K-intercalated Poly(heptazine imide) (Cu SAs/C-K-PHI) photocatalyst with homogeneous bulk co-incorporation of carbon and potassium using a salt-template-induced homogeneous incorporation method.[2,3] The incorporation of Cu single atoms further promotes C-C coupling for C2+ product formation. The synthesized Cu SAs/C-K-PHI photocatalysts exhibits a significantly narrowed band gap (1.79 eV) compared to pristine g-C_3N_4, leading to strong NIR light absorption (> 700 nm) and efficient NIR-photocatalytic activity. Additionally, the Cu SAs/C-K-PHI demonstrates high charge separation efficiency, strong redox capability, and enhanced CO_2 capture and activation ability.[4] Various characterization techniques were employed to analyse the synthesized photocatalysts such as powder X-ray diffraction (PXRD), Attenuated total reflectance-infrared spectroscopy (ATR-IR), and Raman spectroscopy confirmed the crystal structure and structural properties. Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) revealed the optical properties and absorption characteristics. Field emission-scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM) investigated the size, shape, and surface morphology of the photocatalysts. High performance-X-ray photoelectron spectroscopy (HR-XPS) determined the surface elemental composition and chemical states of the elements. Time-resolved photoluminescence (TR-PL) and steady-state photoluminescence (PL) spectroscopies were employed to study the lifetime of photogenerated charge carriers. The photocatalytic CO_2 reduction reaction (PC CO_2RR) performance of the Cu SAs/C-K-PHI is currently under investigation. This work demonstrates a promising approach for developing efficient photocatalysts for the selective conversion of CO_2 into valuable C2+ fuels using sunlight.

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(P-61)

Towards Accurate Determination of Binding Free Energy Using Molecular Dynamics Simulations

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The binding affinity between a protein and its ligand partner has valuable information that plays an important role in predicting medicinal effects in pharmacology. To computationally obtain binding affinity data, several MD-based methods have been developed, and umbrella sampling is one of them. Umbrella sampling is a method of calculating binding affinity through structural changes through sampling along the binding dissociation process. However, it has been reported that the binding affinity hugely depends on the method of sampling. Also, binding affinity can be influenced by other variables, such as initial structure, number of samples, and dissociation path. In this work, we conducted umbrella sampling with different sampling time to explore changes in the potential of mean force (PMF) and its relationship with the number of sampling windows. We found that the PMF was affected by the sampling time. Additionally, we identified a window region that significantly impacted the PMF. These results may help develop a sampling method that allows for efficient and reproducible PMF calculations, reducing the cost and time needed to calculate the binding affinity of many protein-ligand sets.

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(P-62)

Single-Particle Detection by Electronic Resonance Stimulated Raman Scattering (ER-SRS) Microscope

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Electronic resonance SRS (ER-SRS) is theoretically expected to enhance Raman signal up to 100-fold compared to electronic pre-resonance SRS (EPR-SRS)[1]. However, this enhancement was not successfully demonstrated due to significant background interference which mainly includes fluorescence and pump-probe processes[2]. To address this, we utilized a series of small molecules based on 4,9-bis(bis((2-butyloctyl)thio)methylene)-s-indaceno[1,2-b:5,6-b′]dithiophene (referred to as IDSIC, IDSIC-4F, IDSIC-4Cl, and IDSTIC)[3]. These acceptor-doner-acceptor type molecules conjugated to nitrile (-CN) groups have large Raman cross-sections and low quantum yield (<2 %) within the cell-free frequency window (2000-2500 cm^{-1}), resulting in effective signal enhancement. In addition, our unique synchronously pumped double optical parametric oscillator (OPO) instrument allows us to optimize the wavelengths of the pump and Stokes beams to achieve rigorous resonant condition and identify the wavelength combination that provides the highest signal-to-background ratio (S/B). This optimization enabled us to achieve more than 100-fold improvement in the performance of ER-SRS for IDSIC compared to EPR-SRS. We then fabricated polymer dot (Pdot) to further suppress fluorescence through aggregation-induced quenching of fluorescence emission and demonstrated a two-color ER-SRS image of Pdot. The ER-SRS images of IDSIC-4Cl and IDSTIC Pdots at three frequency differences – two of which are resonant to each Pdot while one is off-resonant for both probes – demonstrated crosstalk-free and background-free imaging with high signal-to-noise ratio. We anticipate that the high sensitivity and low background of the resonance Raman-active probe, combined with independent wavelength tuning for S/B optimization, will open a new window for spectral multiplexing in biological imaging.

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(P-63)

Single-Phase High-Entropy Oxide Nanoribbons ($(Co_{1.8}Cr_{0.3}Rh_{0.3}Fe_{0.3}Ni_{0.3})O_4$): A Spinel-Type Electrocatalyst Demonstrating Efficiency and Stability in Oxygen Evolution Through Synergistic Effects

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Sustainable hydrogen production via water electrolysis stands as a promising avenue owing to its zero-carbon footprint, high energy density, and environmental friendliness. However, the sluggish kinetics of the oxygen evolution reaction (OER; $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ at anode) poses a significant bottleneck to overall electrolytic efficiency, stemming from its multi-step electron transfer process. Addressing this challenge, we present the synthesis and characterization of a single-phase high-entropy spinel oxide, $(Co_{1.8}Cr_{0.3}Rh_{0.3}Fe_{0.3}Ni_{0.3})O_4$, leveraging the '*cocktail effect*' to induce synergistic catalytic activity. Following fabrication into nanoribbons through electrospinning and subsequent calcination, a comprehensive analysis of the structural and compositional properties of the high-entropy materials was conducted. Notably, $(Co_{1.8}Cr_{0.3}Rh_{0.3}Fe_{0.3}Ni_{0.3})O_4$, despite its rhodium (Rh) content being less than 10%, demonstrates reduced overpotential and Tafel slope in comparison to commercial benchmark catalyst iridium oxide (IrO_2) under 1 M KOH (*aq*); moreover, it showcases prolonged stability, enduring 12-hours without performance degradation. This study, therefore, underscores the efficacy of high-entropy materials in enhancing OER catalytic performance by augmenting surface-exposed active sites, thus offering insights into advanced electrocatalytic strategies for sustainable electrolysis. This work was financially supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT or by the Ministry of Education (NRF-2021R1F1A1053270).

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Structural characterization of highly crystalline hexagonal perovskite derivative $Sr_6Rh_5O_{15}$ nanofibers

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We report the facile fabrication of hexagonal perovskite-related highly crystalline $Sr_6Rh_5O_{15}$ nanofibers via electrospinning and post thermal annealing process. Perovskite oxides with a general structure of ABO_3 have been extensively studied to date, gaining significant interest due to their versatility in wide applications. Structural distortions in perovskite structures commonly occur due to the size difference in A and B cations, resulting hexagonal perovskites rather than well-known cubic perovskites.[1] $Sr_6Rh_5O_{15}$ is a member of the hexagonal perovskite derivatives with a general formula of $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$ ($m = 1$, $n = 1$), where Sr occupies the A site and Rh occupies both the A′ and B sites.[2] In this work, structural characterizations of the $Sr_6Rh_5O_{15}$ nanofibers were conducted using field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and micro-Raman spectroscopy. This work demonstrated that single-phase $Sr_6Rh_5O_{15}$ was synthesized in highly crystalline form at 900 ℃, with characteristic fibrous morphology. The synthetic methods of highly crystalline perovskite-related material and its characterizations presented in this study are applicable to various fields.

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(P-65)

Fluorescent Protein Charge on Protein Aggregation

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Protein aggregation is a critical phenomenon implicated in various diseases and biological processes[1]. Fluorescent proteins (FPs) are commonly used to label and visualize these aggregations. However, the intrinsic charges of FPs pose significant challenges, as many aggregating proteins are also charged. This charge interaction can lead to artifacts, compromising the accuracy of experimental results. In this study, we systematically examine the impact of FP charge on the aggregation behavior of target proteins. We label model aggregating proteins (TDP43 and FUS) with FPs of varying net charges and analyze the resultant aggregation patterns using advanced fluorescence microscopy techniques. Our findings reveal that the electrostatic interactions between FPs and the target proteins can significantly alter aggregation dynamics, leading to misinterpretation of the aggregation state. We also explore alternative strategies for labeling, such as charge-neutral variants of FPs and site-specific conjugation methods that minimize perturbation of the target protein's native state. These approaches aim to provide more accurate representations of protein aggregation phenomena.

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(P-66)

Pyrene Polyamines: Sensor for Anionic Biomolecules

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The detection of anionic biomolecules is pivotal in understanding various biological processes and developing diagnostic tools. In this study, we synthesized a novel conjugate of polyamine and pyrene designed to facilitate the detection of anionic biomolecules. The polyamine component selectively binds to anionic biomolecules, while the pyrene moiety undergoes excimer formation upon interaction, resulting in fluorescence emission at longer wavelengths. This characteristic fluorescence shift enables the precise detection and quantification of anionic species. We demonstrate the efficacy of our polyamine-pyrene conjugate in various in vitro assays, showcasing its sensitivity and selectivity for anionic biomolecules, such as chitosan, chondroitin 4-sulfate, hyaluronic acid, and heparin. The conjugate's ability to emit at longer wavelengths reduces background interference, enhancing signal clarity and accuracy. Our findings indicate that this dual-functional molecule holds significant promise for applications in biochemical analysis and medical diagnostics, offering a robust tool for the real-time monitoring of anionic biomolecule dynamics.

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The Effects of Positively Charged Polyamines and Metal Ions on Amyloid Beta(1-42) Protein Aggregation

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Amyloid beta (Aβ) aggregation is intricately linked to the pathogenesis of Alzheimer's disease, yet the precise mechanisms remain elusive. In this study, we investigated the influence of positively charged substances, including polyamines and metal ions, on Aβ aggregation. Our findings reveal that Aβ forms both condensates and fibrils under varying conditions, with the nature and extent of these structures modulated by the concentration of the positively charged agents. Notably, the presence of spermine, a polyamine, significantly altered the aggregation profile of Aβ. Increasing spermine concentrations resulted in a decrease in fibril formation concomitant with an increase in condensate formation. A similar trend was observed with magnesium ions, where higher concentrations favored the formation of condensates over fibrils. These results suggest that positively charged substances can differentially regulate the aggregation pathways of Aβ, potentially offering new insights into the molecular mechanisms underpinning Alzheimer's disease.

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Gold Nanoparticle-based Colorimetric Sensing Assay to Detect Charged Proteins

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Intracellular protein condensates, formed through liquid-liquid phase separation, play vital roles in cellular processes and diseases. We present a novel method using polyamine or DNA-conjugated gold nanoparticles (AuNPs) to detect charged protein condensates in cells. AuNPs are conjugated with polyamines or DNA to exploit electrostatic interactions with charged proteins. Polyamine conjugation offers a positively charged interface for binding negatively charged proteins, while DNA conjugation utilizes specific hybridization and negative charge for positively charged proteins. We synthesize stable, monodisperse AuNPs conjugated with polyamines or single-stranded DNA and characterize them using dynamic light scattering (DLS), UV-Vis spectroscopy, and transmission electron microscopy (TEM). Binding interactions between polyamine or DNA-conjugated AuNPs and protein condensates are analyzed using colorimetric assay and fluorescence microscopy. Our findings demonstrate that these conjugated AuNPs specifically and sensitively detect charged protein condensates *in vitro* as well as in cells.

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Electrostatic Modulation of FUS Protein Aggregation by Small Charged Biomolecules

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The development of FUS (FUsed in Sarcoma) protein aggregates, has been identified as a major factor contributing to the development of amyotrophic lateral sclerosis (ALS). The FUS protein, with a net positive charge of +14 e, divided into a negatively charged (-4 e) low complexity domain (LCD) famous as intrinsically disordered region, and a positively charged (+18 e) C-terminal domain (CTD) under physiological conditions. This research argues to uncover how small charged biomolecules are involved in the liquid-liquid phase separation (LLPS) of the FUS protein through electrostatic interactions. Subsequently, LLPS was observed at the negatively charged N-terminus upon the addition of spermine, while the positively charged C-terminus responded to ATP addition. Interestingly, the full-length FUS protein displayed increased LLPS in cells when both ATP and spermidine were present. To prove the mechanism of protein aggregation by electrostatic interaction, a simple further experiment was conducted. The transformation of spermidine from a positively charged state to a neutral charged state, it was confirmed that the degree of LCD aggregation decreased through additional experiments. This study suggests that small charged biomolecules such as ATP and spermidine can bring the LLPS of charged proteins under physiological system.

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Layer-dependent exciton formation in two-dimensional crystals of perylene derivatives

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Organic crystals have garnered attention due to their flexibility, high strength, and their synthesis over large areas using diverse materials. Organic crystals can possess various types of excitons, with interactions occurring between them. In particular, two-dimensional organic crystals with a lower dielectric constant result in high exciton binding energies, making excitons crucial for the photophysical properties and applications of such crystals. Perylene derivatives, such as 3, 4, 9, 10-perylene tetracarboxylic dianhydride (PTCDA), are typical organic semiconductors with a layered structure and high carrier mobility. Although perylene derivatives' exciton formation process has been extensively studied[1], the mixing and conversion between excitons is only roughly known. Here, we observed changes in exciton formation in PTCDA as a function of layer number using time-resolved spectroscopy. We fabricated several layers of PTCDA through physical vapor deposition and determined their exciton lifetimes using time-resolved fluorescence. The appearance of excimers from layer 4 and above, along with a significant decrease in the fluorescence lifetime of charge-transfer excitons (CTE), confirms the conversion of CTE to excimers under specific conditions. This study not only showed the formation of excimers but also quantitatively identified the conditions for their formation. This could facilitate a better understanding of the exciton properties of organic crystals, which may have implications for various optoelectronic device applications, including OLEDs.

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(P-71)

Isomer- and Conformer-Specific Vibrational Spectroscopy of 3-Penten-1-yne (C5H6) Using IR Resonant VUV-MATI Mass Spectroscopy

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3-Penten-1-yne (C_5H_6), a proposed reaction product of propene (CH_2CHCH_3) and the ethynyl radical (C_2H), is a chemical species of interest in astrochemistry, identified in the Taurus Molecular Cloud and on Titan. In this study, we investigated the neutral and cationic states of trans- and cis-3-penten-1-yne using IR resonant VUV-MATI mass spectroscopy. The 3-penten-1-yne sample was synthesized via two different routes to isolate each isomer, and their VUV-MATI spectra were measured. The adiabatic ionization energies were determined to be 9.0499 ± 0.0006 eV for the cis-isomer and 9.0894 ± 0.0006 eV for the trans-isomer based on the origin bands in the MATI spectrum. Quantum chemical calculations were utilized to elucidate the cationic vibrational structures from the VUV-MATI spectrum and the neutral vibrational structures from the IR dip VUV-MATI spectrum. The relative populations of the cis and trans isomers in the 3-penten-1-yne sample were determined using the origin band and Franck-Condon factor analysis, yielding values of 98.3:1.7 and 4.3:95.7, respectively. These findings closely matched the NMR data, providing significant insights into the composition and vibrational behavior of 3-penten-1-yne isomers. Moreover, the study revealed that the main conformation in each isomer adopts the s-trans form under molecular beam conditions, similar to the interstellar medium environment, thereby enhancing our understanding of these species in astrochemical contexts.

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Electron/Hole Capture Coefficient Calculation for $In_xGa_{(1-x)}N$

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Full-color micro-light-emitting diodes (μLEDs), of red, green, and blue emitters, are one of the most promising candidates for next-generation display applications, including near-eye and wearable displays. InGaN-based μLEDs shows high energy efficient in blue and green however red remains challenging. This decrease in efficiency at red wavelengths is attributed to the loss of nonradiative recombination on the exposed surfaces. These losses originate from nonradiative surface states, such as point defects and Ga dangling bonds. Due to high surface-area-to-volume ratios, these effects become ever more important for μLEDs. This decrease in efficiency at red wavelengths is originated from an increased surface-area-to-volume ratio, which increases nonradiative Shockley-Read-Hall (SRH) recombination. The calculation of electron and hole capture coefficient is essential to estimate SRH recombination.

In this study, we calculated the electron capture coefficients and hole capture coefficients of $In_xGa_{(1-x)}N$ (x=0.04, 0.17, 0.25, 0.42) system with density functional theory (DFT). We investigated various types of defect formation energies of $In_xGa_{(1-x)}N$ such as gallium vacancy, indium vacancy, nitrogen vacancy, and carbon substitution on nitrogen sites. We found carbon substitution on nitrogen sites plays more important role in SRH recombination compared to other defects considered through estimation of the transition levels. Our results provide insights into nonradiative recombination and provide guidance for the efficiency reduction analysis of InGaN-based μLEDs at red wavelengths.

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(P-73)

Probing the Vibrational Modes of Hexagonal Ice Employing Resonant Inelastic X-ray Scattering

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Resonant inelastic x-ray scattering (RIXS) provides a powerful technique to probe the vibrational dynamics and local structural environments in condensed matter systems[1]. We conducted high-resolution oxygen K-edge RIXS measurements on ice Ih for both H_2O and D_2O. By analyzing the energy losses from the elastic scattering line, we identified multiple vibrational modes that become populated during the ultrafast core-hole lifetime. These modes encompass the OH stretch, HOH bend, librational motions, and their respective overtones and combinations. Notably, the suppression of overtones and combination modes of librations enabled us to unveil the pure frequency of the HOH bending mode at 1730 cm^{-1}, providing valuable insights into the intricate vibrational behavior and local structure of this crystalline ice form.

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First-Principles Calculations of Direct and Indirect Auger Recombination Coefficients in $In_xGa_{(1-x)}N$

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Recently, indium gallium nitride (InGaN) based micro-LEDs (μLEDs) have gained significant attention due to their potential uses in next-generation high-performance displays. The μLED display technology needs distinct red, green, and blue (RGB) μLEDs as a single pixel for full-color displays. Currently, InGaN materials are used to make blue and green μLEDs, whereas normal-sized aluminum gallium indium phosphide (AlGaInP) is used to make red LED chips. However, when the chip size of AlGaInP LEDs is reduced to micro size, the efficiency drops down dramatically due to high surface recombination and long carrier diffusion lengths.[1] Therefore, extending the emission wavelength of InGaN-based LEDs from blue/green to red is the optimum choice to replace AlGaInP red μLEDs for micro-displays. However, to achieve red emission, the In-content in the quantum wells (QWs) must be more than 30%, which significantly lowers the internal quantum efficiency (IQE) of the μLED.[2] The IQE of InGaN materials across a broad wavelength of the spectrum is limited by defects, carrier leakage, poor hole injection, and Auger recombination. At high current densities, Auger recombination becomes a significant nonradiative loss process as it scales with the cubic power of the free-carrier concentration.[3,4] In this work, we evaluate the direct and indirect Auger recombination coefficients for electron-electron-hole (*eeh*) and hole-hole-electron (*hhe*) recombination processes in a series of $In_xGa_{1-x}N$ (x = 0-0.42) materials by using density functional theory (DFT). We demonstrate that the phonon-assisted indirect Auger processes are more prevalent in GaN than the direct Auger recombination. We find that InGaN alloys exhibit a greater dominance of both direct and indirect Auger processes in comparison to GaN. More importantly, we observe that both the direct and indirect Auger coefficients increase with the increasing In-contents and thus will reduce the IQE. At room temperature, the calculated Auger coefficients of InGaN alloys can be as large as 5.53×10^{-31} cm^6s^{-1}.

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Radiative Recombination Coefficients of $In_xGa_{(1-x)}N$ from First-Principle Calculations

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The InGaN material system has been widely employed for production of light emitting diodes (LEDs), enabling many technologies from general illumination, to display, to high-speed communications. The applications of LEDs, particularly for general lighting utilizing white LEDs, require further improvements in device performance.1,2

The efficiency of optoelectronic materials is fundamentally determined by competition between radiative recombination and non-radiative recombination within the material. III-V semiconductors have huge advantages in optoelectronic applications because of their direct bandgaps which allows greatly improve the probability of radiative recombination.3 Hall proposed a two-band model that can represent the radiative recombination coefficient using band gap, effective mass, and refractive index.4,5 This study aims to calculate the radiative recombination coefficient using Hall two-band model.

In this study, we calculated the radiative recombination coefficient of InxGa(1-x)N (x = 0, 0.04, 0.17, 0.25) materials by using density functional theory (DFT). We considered bandgap value and effective mass of holes and electrons for different In compositions using PBE and PBE sol methods. This study offers valuable insights into the evaluation of radiative recombination based on variation in In composition.

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Experimental observation of a dynamic transition in bulk supercooled water

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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 combining the time-resolved X-ray scattering and evaporative cooling in a vacuum can give a chance to find those properties. Since the X-ray structure factor of water is extremely sensitive to the temperature of water, we utilized the IR pump laser to induce temperature jump and followed the structural relaxation at the new temperature. We successfully measured the dynamics of structural relaxation at the SwissFEL, down to the 228.25 K. In the deeply supercooled regime, especially below 240 K, we found that the dynamics deviate from the previous models describing the fragile liquid, such as Mode Coupling Theory (MCT) and Vogel-Fulcher-Tammann (VFT) equation. This indicates the existence of dynamic transition.

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(P-77)

Electrochemical nitrate reduction via direct eight electron transfer enables high-efficient ammonia synthesis using Zn-nitrate battery by single phase high entropy oxide catalyst

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Electrochemical synthesis of ammonia by nitrate reduction is an efficient approach at low pressure and low temperature compared to conventional Harber-Bosch process. Further, nitrate-based voltaic cells is a highly attractive strategy for reducing the pollutants from wastewater simultaneously producing energy and ammonia. In this work, we have transformed the high entropy spinel oxide into single phase high entropy rock-salt oxide (HEO) by laser irradiation for highly efficient electrochemical nitrate reduction ammonia. Our system contained HEO catalyst produce NH_3 via direct eight electron process with yield 22 mg h^{-1} cm^{-2} at 0.5 V vs. RHE, an impressive NH3 faradaic efficiency (FE) of 92%. Considering the high efficiency reduction process of nitrate to ammonia was further explored in a zinc-nitrate battery system. This battery could be specified by a high output voltage of 1.25 V and exhibit the power density of 1.75 mW cm^{-2} and a high NH_3 FE of 64%. This work demonstrates the effect of high entropy oxide for the NO_3^-RR and provides a promising strategy for NH_3 production and broadening the field of Zn-based batteries.

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(P-78)

NiCoOP on Nickel Foam via Pulsed Laser Irradiation/ Microwave Assisted Processes for Water Oxidation

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In this research, we synthesized NiCoOP on the surface of nickel foam (NF) via pulsed laser irradiation in 1.0 M KOH solution. The laser beam was directed onto the surface of NF, causing it to oxidize and transform into nickel hydroxide ($Ni(OH)_2$). By employing microwaves, it became possible to form NiCo layered double hydroxide (LDH) on the NF surface, a compound challenging to produce through laser irradiation alone. Additionally, NiCoOP/NF was synthesized using a furnace to increase the efficiency of the electrocatalytic performance towards water oxidation. The synthesized materials underwent characterization using FE-SEM, XRD, and XPS analytical techniques and were utilized for the oxygen evolution reaction (OER) in 1.0 M KOH. NiCoOP/NF exhibited superior activity compared to pure NF in the OER. Furthermore, the electrocatalytic activity of NiCoOP/NF was superior to commercial IrO_2 even for long-term water electrolysis performance.

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In Situ Growth of NiFe Layered Double Hydroxide on Nickel Foam via Pulsed Laser for Oxygen Evolution Reaction

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In this study, we developed a new method for fabricating binder-free electrode materials using the pulsed laser irradiation (PLIL) technique. The laser beam was directed onto the surface of nickel foam (NF), causing the NF to oxidize and transform into nickel hydroxide (Ni(OH)2). The use of microwaves enabled the formation of NiFe layered double hydroxide (LDH), a compound that is challenging to produce through laser irradiation alone, on the NF surface. The synthesized materials underwent characterization using XRD, Raman, FE-SEM, and XPS analytical techniques and were utilized for the oxygen evolution reaction (OER). The results demonstrated that NiFe LDH/NF exhibited superior activity compared to pure NF in the OER. The electrochemical results demonstrated that the optimised NiFe LDH/NF catalyst exhibited a low potential of 292 mV at 10 mA cm-2 for the oxygen evolution reaction (OER) in a 1 M KOH solution. This study presents a novel approach to synthesising a highly effective NiFe LDH/NF electrocatalyst for energy-efficient oxygen production.

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(P-80)

Pulsed Laser Ablation-Induced Nickel Sulfo-Selenide as Efficient Electrocatalyst for Furfural Oxidation

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Utilizing electrocatalysis on biomass-derived furfural molecules affords a method for producing valuable feedstocks, offering a robust alternative to the traditionally sluggish oxygen evolution reaction (OER). This study introduces a pulsed laser ablation in liquids (PLAL) approach for synthesizing dianionic sulfur-selenide fused nickel-chalcogenides (NiSSe), facilitating electrochemical OER and furfural oxidation reaction (FOR) in alkaline media. $SeCl_4$ dissolves into Se_2^- and serves as an anionic source via PLAL without requiring a reducing agent. Incorporating Se and S anions into NiSSe modulates the electronic structure of Ni, thereby enhancing its intrinsic electrocatalytic activity and stability for OER, achieving an overpotential of 326 mV at 10 mA/cm^2 and a Tafel slope of 214 mV/dec in 1.0 M KOH. Furthermore, FOR catalyzed over NiSSe produces approximately 13.7 mM furoic acid with a selectivity of ~73.14%, carbon balance of ~89.94%, and a notable Faradaic efficiency of approximately 98.82% over 2 h at 1.58 V vs. Reversible Hydrogen Electrode. In situ electrochemical–Raman spectroscopy identified the formation of NiOOH reactive species through surface restructuring under oxidation potential, acting as a terminal for both water and furfural molecules. This research underscores the effectiveness of the laser-patterned nickel sulfo-selenide in modulating oxidation activity, contributing significantly to the selective valorization of biomass.

Dr. Theerthagiri Jayaraman is a Brain Pool Fellow in Professor Myong Yong Choi's group, Gyeongsang National University, South Korea, since August 2019. His current research focuses on developing electrocatalysts via pulsed laser processes for hydrogen fuel and value-added chemical productions.

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(P-81)

Engineering Carbon-Coated Ruthenium Nanoparticles via Pulsed Laser Ablation for Hydrazine-Assisted Hydrogen Production

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The hydrazine oxidation reaction (HzOR) is a promising alternative to the oxygen evolution reaction (OER) for water electrolysis, enabling the efficient production of green hydrogen energy at low cell voltages. However, the development of efficient bifunctional electrocatalysts that can catalyze both the cathodic hydrogen evolution reaction (HER) and the anodic HzOR in hybrid water electrolysis remains a significant challenge. In this study, we developed carbon-coated face-centered cubic (fcc) ruthenium (Ru) nanoparticles using the pulsed laser ablation in liquid (PLAL) technique. Electrochemical testing revealed that the optimized Ru@C catalyst exhibited a low potential of 61 mV at 10 mA cm^{-2} for the HER in a 1 M KOH solution. Furthermore, it demonstrated a low working potential of -0.032 V at 10 mA cm^{-2} for the HzOR in a 1 M KOH/0.5 M hydrazine solution. These results highlight the excellent bifunctional activity of Ru@C for catalyzing both HER and HzOR, which can be attributed to the highly catalytically active fcc Ru nanoparticles encased in conductive, large surface area, and highly stable carbon layers. Consequently, the overall hydrazine splitting (OHzS) electrolyzer in a two-electrode system saved 1.6 V of energy compared to overall water splitting (OWS). This study presents a novel approach to synthesizing highly active Ru@C electrocatalysts for the production of green hydrogen energy, promoting an environmentally friendly energy source.

About Author: Ms. Heeeun Ahn is a master course student studying under Professor Myong Yong Choi's Team. Her research involves synthesizing nanomaterials efficient for electrochemistry using a pulsed laser system and applying to HER and OER, with the ultimate goal of utilizing for overall water splitting (OWS).

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(P-82)

Laser-Induced Ru/Cu Electrocatalyst for Dual-Side Hydrogen Production and Formic Acid Co-synthesis

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Herein, we report a straightforward approach using pulsed laser technology to synthesize selective hexagonal-close-packed (hcp) Ru nanoparticles attached to Cu nanospheres (Ru/Cu) as bifunctional electrocatalyst for catalyzing the hydrogen evolution reaction (HER) and formaldehyde oxidation reaction (FOR). Initially, Ru-doped CuO flakes were synthesized using a coprecipitation method followed by transformation into Ru/Cu composites through a strategy involving pulsed laser irradiation in liquid. Specifically, the optimized Ru/Cu-4 composite not only demonstrated a low overpotential of 182 mV at 10 mA·cm^{-2} for the HER but also an ultralow working potential of 0.078 mV (vs. reversible hydrogen electrode) for the FOR at the same current density. Remarkably, the FOR‖HER-coupled electrolyzer employing the Ru/Cu-4‖Ru/Cu-4 system achieved H_2 production at both electrodes with a cell voltage of 0.43 V at 10 mA·cm^{-2} while co-synthesizing formic acid. Furthermore, density functional theory analyses elucidated that the superior activity of the Ru/Cu composite originated from optimized adsorption energies of reactive species on the catalyst surfaces during the HER and FOR, facilitated by the synergistic coupling between Ru and Cu. This study presents an alternative strategy for synthesizing highly effective electrocatalytic materials for use in energy-efficient H_2 production with the cosynthesis of value-added chemicals suitable for practical applications.

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Pulsed Laser Stabilization of Ru Nanoclusters on CuS Electrocatalysts for Boosted Hydrogen Production and Value-added Sulfur Co-Generation

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Hybrid water electrolysis using a sulfion oxidation reaction (SOR) provides a distinctive approach to minimizing the power consumption of hydrogen production whereas addressing ecological pollution issues. Despite this, the development of efficient dual-functional catalysts for both SOR and the hydrogen evolution reaction (HER) remains essential. In this study, we introduce a simple and quick approach to synthesize a CuS/Ru composite that functions as a dual-functional electrocatalyst, increasing hydrogen production and converting sulfion into valuable sulfur products. The composite consists of Ru nanoclusters supported on a CuS nanostructure, created through simple pulsed laser irradiation in liquid under ambient conditions. The designed CuS/Ru-30 electrocatalyst demonstrates outstanding performance, with a low overpotential of 182 mV for HER and a small working potential of 0.28 V (vs. RHE) for anodic SOR, achieving a current density of 10 mA cm^{-2}, while maintaining outstanding stability. Furthermore, the CuS/Ru-30 electrocatalyst exhibits high selectivity for converting sulfion to valuable sulfur during anodic oxidation. In a two-electrode electrolyzer system with CuS/Ru-30 as both the cathode and anode, the coupled water-splitting system requires only 0.52 V to achieve 10 mA cm^{-2}, which is significantly lower than the 1.85 V required for overall water splitting. This study describes a quick and easy method for creating a bifunctional electrocatalyst that is efficient for hydrogen production and facilitates the recovery of valuable sulfur sources.

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Electrocatalytic Nitrate Reduction to Ammonia Synthesis via Pulsed Laser produced $Ag/Ag_2O/CuO$ Composite

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Nitrogen fertilizers are essential for global food security, but their production through the Haber-Bosch process is energy-intensive and reliant on fossil fuels. This process consumes 1-2% of the world's energy and contributes about 1.5% of global CO_2 emissions. Overuse of nitrogen fertilizers also increases nitrate concentrations in groundwater, causing environmental issues. Sustainable and energy-efficient ammonia production methods are urgently needed to address these challenges. This study focused on synthesizing an $Ag/Ag_2O/CuO$ composite using a simple and rapid pulsed laser ablation method. The synthesized composite was utilized as an efficient electrocatalyst for the nitrate reduction reaction (NO_3RR). Electrochemical analysis confirmed that the $Ag/Ag_2O/CuO$ catalyst exhibited a faradaic efficiency of 89% at -0.3 V vs. RHE and an ammonia yield of 2.95 mg h^{-1} mg^{-1}. Additionally, the performance of a Zn-nitrate battery was evaluated, showing a power density of 5.085 mW cm^{-2} and a faradaic efficiency of 55% at 6 mA cm^{-2}. This study significantly contributes to the development of strategies for synthesizing potential catalysts for large-scale ammonia production.

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High-Entropy Single-Atom Site Incorporated FeRuPtNiCoPd Alloy on Graphene Oxide for Enhanced Electrochemical Water Splitting

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The study investigates the incorporation of high-entropy single-atom sites, comprising six distinct elements to form a single-phase FeRuPtNiCoPd alloy supported on graphene oxide. This synthesis method involves pulsed laser irradiation in liquid. The resulting HESA and HEA framework offer a tailored surface configuration and diverse active sites, facilitating electrochemical total water splitting (OWS) [1]. Material characterization was conducted using various characterization techniques such as scanning electron microscopy, Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy. The synergistic intrinsic interactions within the high-entropy system, combined with the rapid photoreduction of Fe^{2+} ions, result in enhanced active site density compared to Fe^{3+} ions, particularly evident in the HER activity in 0.5 M H_2SO_4 and OER activity in 1.0 M KOH. Notably, the optimized HESA-HEA/GO-Fe^{2+} catalyst demonstrates superior OWS performance across a wide pH range with lower cell voltage compared to HESA-HEA/GO-Fe^{3+} and commercial Pt/C catalysts.

About Author: Ms. Yeryeong Lee is currently pursuing a PhD course at GNU under the supervision of Professor Myong Yong Choi. Her research includes the synthesis of electrocatalytic nanomaterials using pulsed laser technology for HER, OER, and water splitting applications.

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(P-86)

Characterization of BODIPY Applying Competitive Effects of Photoinduced Charge Transfer and Heavy Atom Effects for Cell Imaging and Photodynamic Therapy

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Photodynamic therapy (PDT) in combination with cell imaging-based diagnosis, in other words, imaging-guided PDT (IgPDT) is an attractive cancer treatment modality due to high therapeutic accuracy and low side effects. As part of ongoing efforts to develop fluorescent triplet photosensitizers (PSs) for clinical use in IgPDT, herein we report the synthesis and spectroscopic, theoretical, and *in vitro* characterization of pyridinium-substituted halogenated boron dipyrromethene (BODIPY) dyes (PyB*X*I, X = H, M, Br). We revealed that the incorporation of cationic pyridinium, styryl moieties, and triethylene glycol (TEG) chains on the innate BODIPY structure enabled the resultant PyB*X*I dyes to display desirable properties, including mitochondria-targeting ability, absorption and fluorescence within the phototherapeutic window (650–850 nm), and water solubility. The pyridinium group facilitated the formation of charge transfer (CT) states following photoexcitation, which, instead of mediating triplet state formation as proposed previously, resulted in unfavorable nonradiative decay processes. Nevertheless, the halogenation enhanced the intersystem crossing, rendering PyBMI and PyBBrI to exhibit improved singlet oxygen generation capabilities compared to that for PyBHI. *In vitro* experiments using MCF-7 and HeLa cells revealed that PyBBrI dyes exhibited a mitochondria-targeting ability, which may have facilitated their accumulation in the cytoplasm of the cancer cells and NIR fluorescence sufficient for cell imaging. Furthermore, PyBBrI dyes showed a high photocytotoxicity, with half maximal inhibitory concentration (IC_{50}) values of 96 nM and 219 nM for MCF-7 and HeLa cells, respectively. Overall, we have successfully shown the synthesis and characterization of BODIPY-based theragnostic agents, which may contribute to developing strategies for the design of novel PSs applicable to practical cancer treatment.

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(P-87)

Synthesis and Post-synthetic Treatment of Blue-Emitting $CsPbBr_3$ Nanoplatelets with Tunable Thickness

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Lead halide perovskite [$APbX_3$; A = Cs, methylammonium (MA), or formamidinium (FA); X = Cl, Br, or I] nanocrystals (NCs) have attracted significant attention for their potential applications in optoelectronic devices including photovoltaics, photodetectors and light-emitting diodes (LEDs), owing to their low-cost solution processability and outstanding photophysical properties. Among them, colloidal cesium lead halide ($CsPbX_3$) perovskite NCs exhibit appealing properties such as broad absorption with a high absorption cross-section, high photoluminescence quantum yield (PLQY), emission with a narrow full width at half maximum (FWHM), and a tunable band gap in the entire visible range, making them extremely promising materials for light-emitting applications. While the conditions for utilization have been fully met by NCs emitting in the red and green spectral ranges, those in the blue range still require improvements in PL emission efficiency and stability. In order to generate blue-emitting $CsPbX_3$ NCs, the conventional approaches of using small-sized $CsPbBr_3$ NC (<5 nm) and adjusting the halogen composition (Br/Cl ratio) suffer from constraints in broad emission spectra and phase separation, respectively. In this poster, we present a facile room-temperature synthesis method that allows for precise thickness control to obtain two-dimensional $CsPbBr_3$ nanoplatelets (NPls). NPls with thicknesses of 6, 4, and 2 monolayers (MLs) were obtained by simply controlling the ratio of Cs/Pb precursors and the amount of added acetone, which exhibited narrow PL emission with a tunable wavelength from 505 to 435 nm due to the quantum confinement effect. Furthermore, we performed post-synthetic treatment using the $PbBr_2$ solution and demonstrated that it considerably increased the PLQY of all NPls while causing a negligible change in the PL emission peak. The effect of treatment was more pronounced for thinner NPls, resulting in PLQY increases of up to five times. These results are assumed to be the addition of $PbBr_2$ solution, which reduces trap states associated with surface defects such as lead and bromide vacancies induced by the high surface-to-volume ratio of the NPls.

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(P-88)

Single-Particle Photophysical Study on the Effect of $MgBr_2$ Post-Treatment of $CsPbBr_3$ Perovskite Quantum Dots

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The presence of localized trap states on the surface of cesium lead halide ($CsPbX_3$) perovskite quantum dots (PQDs) is one of the greatest obstacles to the commercialization of perovskite-based optoelectronic and photovoltaic devices. Surface passivation by post-synthetic metal halide treatment is considered a promising strategy to suppress surface defects in inorganic lead halide perovskites and elevate the efficiency of devices based on these materials. Herein, we synthesize $CsPbBr_3$ PQDs by ligand-assisted reprecipitation (LARP) method and develop a facile ambient post-synthetic $MgBr_2$ treatment protocol. Following $MgBr_2$ doping, we measure narrower full width at half maximum (FWHM), and higher photoluminescence quantum yield (PLQY) than pristine $CsPbBr_3$ PQDs. We investigate PL blinking at a single particle level using a home-built laser scanning confocal fluorescence microscope to elucidate the degree of defects changed by doping and the correlation between trap states and charge carrier recombination. As a result of doping, Mg-doped $CsPbBr_3$ PQDs show improved PL lifetimes (τ) and longer duration of ON-states (τ_{ON}), indicating the effective suppression of surface traps. Our experimental results provide an insightful understanding of the passivating roles of $MgBr_2$ on the surface of $CsPbBr_3$ PQDs.

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(P-89)

Unveiling Photophysical Properties of Sb-doped Cesium Lead Bromide ($CsPbBr_3$) Perovskite Quantum Dots via Single Particle Fluorescence Spectroscopy

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All inorganic cesium lead halide $CsPbX_3$ (X = Cl, Br, and I) perovskite quantum dots (PQDs) have emerged as promising material due to their surpassing fluorescence properties such as tunable bandgap, long-range mobility of charge carriers, and high photoluminescence quantum yield (PLQY). However, despite the exceptional performance of PQDs, their sensitivity to ambient conditions, including air, moisture, and heat, can result in stability issues attributed to various defects, potentially limiting their applications. Doping a different metal ion instead of the Pb site is one of the various methods explored to address these issues. This strategy offers insights into mitigating the impact of defects within the PQD lattice, thereby enhancing its performance. To overcome the limitations of PQDs, it is crucial to conduct research on the charge carrier dynamics of PQDs, employing applied strategies for performance improvement such as metal-ion-doping. To unravel the charge carrier dynamics associated with trap states in these metal-ion-doped PQDs, conducting PL measurements at single-particle is imperative. In this study, to precisely elucidate the impact of Sb doping on the charge recombination process, we investigated the photophysical properties of the two types of PQDs at the single-particle scale using a custom-built laser scanning confocal microscope system. We synthesized native PQDs and Sb-doped PQDs at room temperature using the widely employed ligand assisted re-precipitation (LARP) method and subsequently confirmed their fundamental properties. We compared the influence of trap states on the charge recombination process depending on whether Sb-doped or not based on the statistical distributions of on- and off-time fractions and relative trapping and de-trapping rates derived from PL blinking behavior of each PQD. Through this, we demonstrate a reduction in the influence of trap states, the cause of PL quenching, on the charge recombination process, indicating that Sb doping can suppress defects within PQDs.

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(P-90)

Solar CO_2 Reduction to Liquid Fuels using Nafion/PVP/rGO/NiO/CeO_2 @SiO_2@Fe_3O_4 Hybrid Composite Photocatalyst

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To mitigate global warming, there are so many approaches to reduce CO_2 in the air. As one of the promising CO_2 reduction methods, photocatalysts attract much interest because they can utilize solar radiation as an energy source, thus enabling low-cost utilization. For continuous flow CO_2 reduction using photocatalysts, an additional separation process is necessary, which in turn requires increased energy consumption and additional facilities. To address this issue, we introduced fast and energy-efficient magnetic separation to the catalyst by creating a core-shell structure. Nafion/PVP/rGO/NiO/CeO_2@SiO_2@Fe_3O_4 (NPRNCSF) hybrid composite microspheres, fabricated through a layer-by-layer coating process. First, Fe_3O_4 is used as the core for magnetic separation due to its magnetic properties [1]. To avoid direct contact between the photocatalyst layer and Fe_3O_4 core, which could reduce the efficiency of CO_2 reduction, a SiO_2 layer is formed onto the Fe_3O_4 using the modified Stöber method. The (Nafion/PVP/rGO/NiO/CeO_2) photocatalyst layer is formed on the SiO_2@Fe_3O_4 core [3-4]. Oxygen vacancies present in the CeO_2 catalyst layer enable the adsorption and activation of CO_2, enhancing the rate and efficiency of CO_2 reduction. Utilizing a p-n junction comprising NiO and CeO_2 by interface engineering enhances charge separation by suppressing charge recombination, thereby prolonging the lifetime of photoexcited electrons and increasing CO_2 reduction efficiency. To facilitate the reduction of CO_2 to formaldehyde, rGO is grafted onto the NiO/CeO_2 heterostructure photocatalysts, facilitating multi-electron transfer processes. The PVP layer introduced to capture and activate stable CO_2 molecules. And Nafion layer is used for proton transfer. After CO_2 reduction experiments using catalysts, resulting reduction products were measured to evaluate the efficiency of CO_2 reduction and selectivity of the products.

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(P-91)

Excited state dynamics of Donor-π-Acceptor fluorescent dye with different functional groups

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Dithiophene-conjugated benzothiazole derivative (DTBz), featuring thiophenol as an electron donor and ethyl ester as an electron acceptor linked by a π-conjugated backbone, is a donor- π-acceptor fluorescent dye with high quantum yields in various organic solvents. Despite a weak solvatochromic effect, DTBz exhibits bright emission around 480 nm under 390 nm excitation. Notably, in polar solvents, and additional intramolecular charge transfer (ICT) state emission band appears around 640 nm, particularly intense in DMSO. The excited state dynamics of DTBz were revealed via femtosecond transient absorption spectroscopy and time-resolved photoluminescence measurements and its analysis. Moving forward, the contribution of the ICT state to excited state relaxation pathways is expected to vary with changes in molecular electron density. Compared to the ethyl ester terminal group, hydrogen is less electron-withdrawing, while carboxylic acid is more so. By altering the ester moiety to hydrogen and carboxylic acid, while maintaining the same π-conjugation scaffold of DTBz, this study aims to provide insights into the effects of electron density on the excited state dynamics

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(P-92)

Insights into the Robust Electrocatalytic Activity of Laser-Made Pd/$NiCo_2O_4$ Composite for Simultaneous Hydrogen Production and Hydrazine Degradation

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Recent research has been focused on utilizing the hydrazine oxidation reaction (HzOR) instead of the slower anodic oxygen evolution reaction (OER) in water electrolysis to enhance hydrogen production efficiency. Developing highly efficient bifunctional electrocatalysts capable of catalyzing both the hydrogen evolution reaction (HER) and HzOR is essential for cost-effective fabrication of high-performance water electrolyzers. In this investigation, we synthesized Pd nanoparticles decorated on $NiCo_2O_4$ nanoplates to serve as a bifunctional electrocatalyst. The synthesis process involved generating $NiCo_2O_4$ nanoplates through a combination of hydrothermal reaction and high-temperature calcination. Subsequently, the Pd/$NiCo_2O_4$ composite was obtained by decorating Pd nanoparticles onto the $NiCo_2O_4$ nanoplates using the pulsed laser irradiation (PLI) method. The best Pd/$NiCo_2O_4$ composite demonstrated remarkable electrocatalytic performance, with a low overpotential of 294 mV for HER and an ultra-small working potential of −6 mV (vs. RHE) for HzOR at 10 mA cm^{-2} in a 1 M KOH electrolyte. Consequently, an overall hydrazine splitting (OHzS) electrolyzer utilizing the Pd/$NiCo_2O_4$‖Pd/$NiCo_2O_4$ system consumed low cell voltages of 0.35 V and 0.94 V to deliver current densities of 10 mA cm^{-2} and 100 mA cm^{-2}, respectively. This study presents a straightforward approach for engineering bifunctional electrocatalysts suitable for energy-efficient hydrogen production.

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(P-93)

Laser-induced Flower-like Bimetallic CuCo-Sulfides from CuCo Prussian Blue Analogues for Enhanced Nitrite Reduction to Ammonia

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Examining the catalyst formation mechanism and producing precisely controlled catalysts are indispensable aspects of materials and catalytic chemistry. In this study, flower-shaped CuCo sulfides were synthesized using bimetallic CuCo Prussian blue analogs (PBA) via a pulse laser irradiation (PLI) process. Real-time confirmation of sulfide formation by PLI was achieved through Raman spectroscopy using an acoustic resonance device. The catalytic potential of these sulfides in the nitrite reduction reaction (NRR) was demonstrated. Initially, sulfur decomposed by the laser combined with the CN groups of PBA to form thiocyanate, followed by rapid reactions with copper to produce Cu_2S and subsequent reactions with cobalt to form Co_9S_8. Moreover, the correlation between the sulfide shapes and laser parameters was observed, indicating the influence of laser parameters on the formation mechanism. Additionally, well-defined and tunable CuCo sulfides exhibited remarkable results in selectively reducing nitrite to produce ammonia. This study contributes to enhancing the selectivity of controlled catalyst synthesis and providing efficient electrocatalysts for nitrite reduction to ammonia.

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(P-94)

Enhanced Oxygen Evolution Kinetics of CO_2 Laser-Produced high Entropy Oxide Electrocatalyst for Efficient Hydrogen Production

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Water electrolysis is regarded as a promising strategy for clean hydrogen fuel production, utilizing renewable energy sources to split water molecules without releasing any toxic byproducts. However, the large-scale application of water electrolysis faces significant hurdles due to the high overpotential required for the anodic oxygen evolution reaction (OER), mainly attributed to the lack of efficient electrocatalysts for OER. In this study, we designed and synthesized a spinel-structure $Cr(NiFeCoV)_2O_4$ high-entropy oxide (HEO) using a novel and rapid CO_2 laser strategy. The synthesized $Cr(NiFeCoV)_2O_4$ HEO exhibited superior OER performance, with a lower overpotential of 278 mV at 10 mA cm^{-2} compared to both bimetallic $CrCo_2O_4$ (398 mV) and benchmark IrO_2 (369 mV) in a 1 M KOH electrolyte. Additionally, the $Cr(NiFeCoV)_2O_4$ HEO catalyst demonstrated long-term stability over 100 h. Notably, an alkaline water electrolyzer with a $Cr(NiFeCoV)_2O_4$ (+)||Pt/C(–) couple required a minimum cell voltage of only 1.57 V to supply 10 mA cm^{-2}, compared to 1.61 V for an IrO_2 (+)||Pt/C(–) electrolyzer. This work introduces a new method for the development of highly efficient and durable OER electrocatalysts for efficient hydrogen production.

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(P-95)

Pulsed Laser Synthesis of Multicomponent High-Entropy Alloys for Electrocatalytic Nitrite Reduction to Ammonia Synthesis

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Ammonia (NH_3) stands out as a carbon-free fuel and is crucial for producing chemicals like fertilizers. Converting toxic nitrite ions (NO_2^-) from contaminated water to NH_3 in an electrocatalytic system holds significant environmental and sustainable promise. Moreover, this system has the potential to transition from being energy-intensive to energy-generating. In this study, we synthesized low-to-high entropy alloys using pulsed laser techniques. Leveraging innovative pulsed laser technology, we were able to synthesize alloys ranging from low entropy to high entropy by adjusting the number of elements involved. High entropy alloys (HEAs) exhibited remarkable performance in the nitrite reduction reaction (NO_2RR) due to their diverse active sites and structural flexibility. These attributes optimize interactions with reactants and enhance catalytic efficiency. In a 0.5 M Na_2SO_4 solution containing 0.1 M $NaNO_2$, the freestanding HEA electrode achieved a high faradaic efficiency (FE) of 86.75% at -0.6 V vs. RHE, demonstrating excellent stability. Additionally, the assembled Zn–NO_2^- battery displayed a power density of 3.87 mW cm^{-2} and the highest NH_3 FE of 90.7%. This research not only paves the way for the Zn–NO_2^- battery system for sustainable energy supply and NH_3 electrosynthesis but also presents an attractive electrocatalytic approach for the degradation of NO_2^- pollutants in wastewater. Overall, this study significantly contributes to the design and development of efficient, stable electrocatalysts via laser technology, facilitating the electrocatalytic production of ammonia while addressing nitrite waste in wastewater.

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Time-Resolved Spectroscopic Study of a Series of Ligand-Conjugated Ir-Re Photocatalysts

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The process of photo-conversion of CO_2 to the energy-rich compounds in a photocatalytic system occurs in a wide time range, from picoseconds to minutes. Moreover, electron transfer (ET) dynamics during this process are often complicated because inter/intramolecular and multi-electron transfers are involved in photocatalytic reactions. In our previous study, the intramolecular ETs from photosensitizer (PS) to photocatalyst (PC) have been observed in the bimetallic Ir-Re photocatalysts, happening through rotatable bridging ligands (BL). Here, we studied a new series of bimetallic Ir-Re supramolecular systems where two metal parts are connected through rotation-restricted ligands, bipyrimidine (bpm) and dipyridinyl pyrazine (dpp). Contrary to the expectation of having better ET for CO_2 conversion, these systems do not act as a CO_2 photocatalyst, showing no CO_2 conversion efficiency. We performed femtosecond transient absorption (TA) and picosecond-resolved fluorescence spectroscopies to investigate ET dynamics in these systems. With the help of global analysis and quantum calculations, we tried to unravel the mechanism behind their low efficiency, which can provide us with valuable insights into developing better photocatalytic systems.

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(P-97)

Ionic Liquid Dynamics in Ion Gel Probed by Dynamic Stokes Shifts of a Coumarin Dye

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Ion gel is a polymer film which is filled with ionic liquid (IL). Ion gel is attracting much attention as an alternative of liquid electrolyte that is used in rechargeable battery due to its high electric conductivity and stability. To develop efficient ion gels, it’s necessary to understand the mechanisms of electron and ion transfers and their dynamics. However, there are not many reported studies of reaction dynamics in gel phase and its detailed mechanisms. Hence, in this study, we prepare ion gels consisting of three types of IL (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (CnmimNTf2, n = 2, 4, 6: ethyl-Emim; butyl-Bmim; hexyl-Hmim)) and polymer(poly(ethylene glycol) diacrylate)) to investigate the IL-dynamics, using time-resolved fluorescence spectroscopy. In particular, we analyzed dynamic stokes shift of coumarin in the gels to reveal solvation dynamics of IL. As a result, the IL-dynamics in the gels are much slower than those in the bulk IL. Moreover, we found that the composition of the polymer significantly affects the dynamics. According to these results, the IL-dynamics in the ion gels are influenced by inner structure of ion gel. We are currently investigating the IL-dynamics in different ion gels.

(P-98)

Remotely Modulating the Optical Properties of Organic Charge-Transfer Crystallites via Molecular Packing

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Organic charge-transfer complex (CTC) formation has emerged as an effective molecular engineering strategy for achieving the desired optical properties via intermolecular interactions [1-4]. By synthesizing organic CTCs with carbazole-based electron donors and a 7,7,8,8-tetracyanoquinodimethane (TCNQ) acceptor and adopting a molecular linker located remotely from the charge-transfer interface within the donors, we were able to modulate near-infrared absorptive and short-wavelength infrared emissive properties. Structural characterizations performed using single-crystal X-ray diffraction confirmed that the unique molecular arrangements induced by the steric hindrance from the remotely located linker significantly influence the electronic interactions between the donor and acceptor molecules, resulting in different photophysical properties. Our findings offer an improved understanding of the interplay between molecular packing and optoelectronic properties, providing a foundation for designing advanced materials for optoelectronic applications.

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(P-99)

Solid Acid Catalyst Screening for Catalytic Pyrolysis via Thermogravimetric Analysis (TGA) of Low Density Polyethylene (LDPE) Degradation

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Numerous numbers of plastics like low density polyethylene (LDPE) have been produced and exploited for various usage thanks to its various advantages such as lightweight, chemical resistance, durability, etc. However, due to the absence of appropriate treatment method of surplus waste plastic, it has caused severe environmental issues. [1] Low temperature thermal degradation of waste plastic in N_2 atmosphere, has been considered as an adequate breakthrough, but large energy consumption still remains as the main bottleneck of this technology. Therefore, catalytic degradation, which is implementing with catalyst decreasing activation energy and bond dissociation energy, has emerged as a new resolution. [2] In this study, TGA for pure LDPE and LDPE with four common solid acid catalyst α-Al_2O_3, γ-Al_2O_3, amorphous silica-alumina (ASA) and silica-alumina (SA) with different heating rates 5°C/min, 10°C/min, and 20°C/min were carried out to compare the degradation performance. Also, catalyst characterization via XRD and BET were implemented to investigate the systematic role of each catalyst for the pyrolysis of LDPE. LDPE with ASA and 5°C/min heating rate showed the lowest final degradation temperature at 420°C. Through XRD and BET analysis, ASA showed the largest surface area as 489 m^2/g and the most amorphous crystal structure compared to other three catalysts. Also, activation energy calculation for 5 thermal degradation reaction temperature was implemented. Activation energy of pure LDPE and LDPE with ASA catalyst (LDPE : ASA = 1:9) were 159.9 KJ/mol and 88.3 KJ/mol with 10°C/min heating rate condition, respectively.

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Young-ho Jeong, a researcher at the Korea Institute of Energy Technology (KENTECH)'s Carbon Neutrality Climate Technology Lab, is dedicated to developing waste plastic degradation technology aimed at low-temperature degradation and product selectivity.

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(P-100)

DFT Study: Heme compound II models in chemoselectivity and disproportionation reactions

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Heme compound II models were synthesized from electron-deficient and -rich porphyrin, $[Fe^{IV}(O)(TPFPP)(Cl)]^-$ (**1a**) and $[Fe^{IV}(O)(TMP)(Cl)]^-$ (**2a**), respectively (TPFPP = *meso-tetrakis(pentafluorophenyl)porphyrinato dianion*, TMP = *meso-tetrakis(2,4,6-trimethylphenyl)porphyrinato dianion*). Experimentally, **1a** formed 2-cyclohexen-1-ol as a product in cyclohexene oxidation reaction with a high Kinetic Isotope Effect (KIE) of 41. In contrast, **2a** formed a cyclohexene oxide product with a low KIE value of 1. This suggests that with **2a**, C=C epoxidation is preferred and behaves more like Heme compound I models. These results suggest that **2a** is involved in a disproportionation reaction to form $[Fe^{IV}(O)(TMP^{+\bullet})]$ (**2b**), a compound I model, whereas **1a** does not show any preference for a disproportionation reaction under the same reaction conditions. To support these results, DFT calculations were performed, and the results support that the Compound II model **1a** prefers C-H bond hydroxylation, and the disproportionation reaction is thermodynamically controlled by the porphyrin ligands.

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(P-101)

Implementation of Qiskit-BAGEL interface for excited state quantum simulations: Demonstration on State-averaged orbital-optimized variational quantum eigensolver (SA-OO-VQE)

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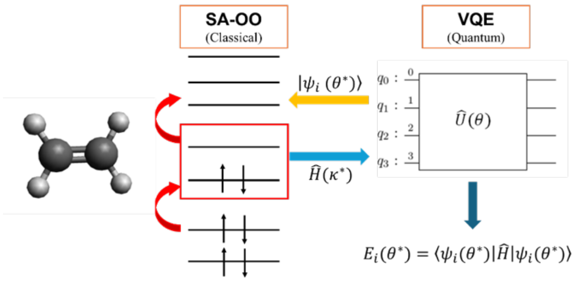
The variational quantum eigensolver (VQE)[1] is one of the most efficient methods for quantum chemical computation using noisy intermediate-scale quantum (NISQ) devices. VQE is a hybrid quantum-classical algorithm which employs both quantum and classical devices. Methods such as subspace-search VQE (SSVQE) and variational quantum deflation (VQD) are also developed to compute the electronic structures of excited states. To use active spaces and consider additional electron correlation energy, state-averaged orbital-optimized VQE (SA-OO-VQE),[2,3] which is motivated by the state-averaged complete active space (SA-CASSCF) method, is introduced.

In this work, we have reproduced SA-OO-VQE algorithm by interfacing two software packages IBM Qiskit and BAGEL,[4] which are used for quantum and classical calculations, respectively. We have tested this algorithm to calculate the lowest three singlets using unitary coupled cluster singles and doubles (UCCSD) ansatz. To demonstrate the utility of the current implementation, we computed SA-OO-VQE energies for four small molecules (Molecular Hydrogen, Lithium hydride, Ethylene, Methanimine) with (2*e*,2*o*) active spaces. Because the BAGEL package is powerful in calculating correlated electronic structures, we anticipate that this interface can be utilized to compute correlated systems using quantum simulators.



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(P-102)

Efficient One-Pot Synthesis of PdAgCu Wormlike Nanoparticles for Enhanced Ethanol Oxidation Catalysis

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Nanoparticle catalysts are increasingly utilized for enhancing green energy conversion, aiding in the development of sustainable solutions [1,2]. While precious metals have traditionally been employed to ensure nanoparticle stability, their high cost presents a significant economic drawback. To address this, we explored the use of nanoparticle alloys to boost both stability and catalytic activity, while incorporating copper (Cu) to improve cost-effectiveness. In this study, we synthesized PdAgCu (palladium-silver-copper) wormlike nanoparticles (Figure 1). The synthesis was conducted at 90°C for 2 hours using cetyltrimethylammonium chloride (CTAC) as the surfactant and hydrazine as the reducing agent. The electrochemical properties of these nanoparticles were then evaluated using cyclic voltammetry (CV) in a 0.1M KOH solution. Additionally, the catalytic activity and stability were assessed through the ethanol oxidation reaction in a mixed solution of 0.5M ethanol and 0.1M KOH.

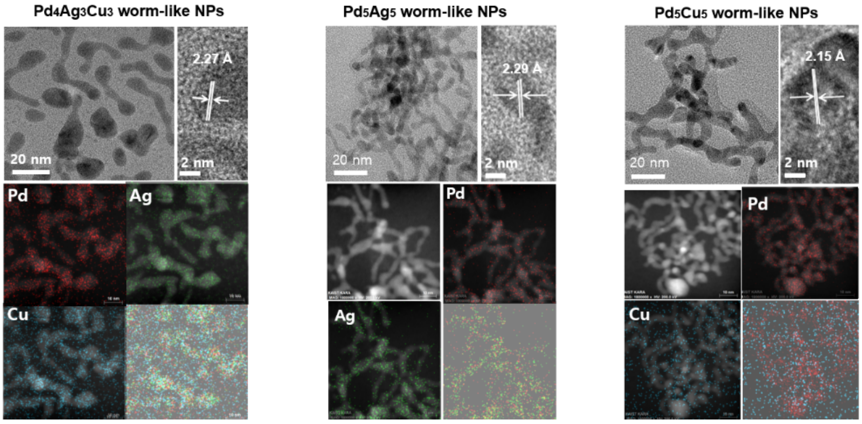

Figure 1. TEM Image of wormlikes and EDS mapping with PdAgCu, PdAg and PdCu

Keywords: PdAgCu wormlike, Ethanol oxidation

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(P-103)

Solvation Dynamics of Ionic Liquid in Various Sized Pores of Supported Ionic Liquid Membranes

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Room temperature ionic liquids (RTILs) are salts that are liquid at room temperature and are attracting much attention in the field of carbon capture due to their high CO_2 solubility. However, separating dissolved CO_2 in RTILs requires high energy, and the utilization of bare RTILs is costly and inefficient. Advanced technologies combining ionic liquids (ILs) and membranes, such as supported ionic liquid membranes (SILMs), have emerged to improve efficiency. In SILMs, CO_2 gas is captured in ILs impregnated in the pores and is separated by a diffusion process. Therefore, they are highly energy efficient and can provide high selectivity while consuming relatively little solvent. To develop better SILMs for carbon capture and separation, it is important to clarify the reaction dynamics inside their pores.

In this study, the solvation dynamics of ionic liquids in supported ionic liquid membranes (SILMs) with a pore size of 0.02, 0.1, and 0.2 microns are identified using time-resolved fluorescence spectroscopy. We prepared the SILMs with the combination of anodisc membrances and imidazolium-based ILs and measured the dynamic stokes shifts of a C153 dye in SILMs to reveal the solvation dynamics of IL. We compare the IL dynamics measured in different pore sizes and different lengths of the cation's alkyl chain to deduce the effects of these parameters on the dynamics.

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(P-104)

Polarization-Dependent Plasmon Coupling in Gold Nanorod–Nanosphere Assemblies

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Gold nanoparticles (AuNPs) have unique properties such as bright visible color, creation of localized electric fields, generation of hot charge carriers, and emission of heat.[1] Plasmons, collective oscillation of free electrons, are at the heart of all of these phenomena. When two or more AuNPs are in close proximity, their plasmons are coupled and form hybridized modes.[2] Gold nanorods (AuNRs), as an anisotropic nanostructure, are assembled with gold nanospheres (AuNSs) into a shape of core@satellites nanoassemblies. In previous study, we have demonstrated that as AuNSs attach to the end or side of AuNRs, plasmon coupling occurs selectively to longitudinal plasmon coupling mode (LO coupling mode) or transverse plasmon coupling mode (TR coupling mode) of AuNRs, respectively.[3] Here we investigate how plasmon coupling occurs, depending on the polarization of incident light for anisotropic nanoparticles combined with nanospheres. Polarization-dependent scattering spectra for individual nanoparticles are measured using a dark-field microscope, combined with a spectrometer. In the scattering spectra, we observe only a single peak at 623 nm, assigned to the LO mode of a AuNR; no peak for the TR mode. The scattering spectra of the assembly for unpolarized light exhibits a strong peak at 737 nm and a broad shoulder peak near 650 nm. The main peak is shifted from 623 nm to 737 nm and assigned to the coupling of the LO mode. The broad peak is likely shifted from the TR mode of AuNR. When the polarization of incident light varies, the intensity of the LO coupling mode or the TR coupling mode falls and rises. Polarization-dependent dark-field single-particle scattering spectra reveal that the LO coupling mode is preferentially supported by light polarized along the long axis of the AuNR. In contrast, the TR mode is weak in intensity and does not show strong dependence on the polarization angle of light. A simulation study confirms that plasmon coupling in a transverse direction for AuNR@AuNS is sensitive to the symmetry of the assembly. This study deepens an understanding of how polarized light interacts with plasmons.

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(P-105)

Exploring Carbon-Halogen Bond Activation Pathways with $[Au_2(dppm)_2]Cl_2$ Photocatalyst via Time-Resolved X-ray Solution Scattering

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The formation of a carbon-carbon bond is one of the most important subjects in organic chemistry. One critical avenue toward this goal involves the activation of carbon-halogen (C-X) bonds. Dimeric Au catalysts have emerged as a promising reagent, which can replace the hazardous or toxic reagents and Ru- or Ir-based photoredox catalysts which have limited reduction potential. Despite of its versatility, the mechanism of C-X activation and the role of the dimeric Au catalyst during the process remain ambiguous. (1, 2) Here, we applied time-resolved X-ray solution scattering (TR-XSS) to elucidate the intermediates generated during the reaction and its explicit structure, and finally present the reaction mechanism. (3) In previously suggested quenching event, molecules should encounter each other through translational diffusion process. (4, 5) However, the time-resolved scattering pattern at 100 ps (Figure 1) suggests the presence of a faster conversion process occurring before 100 ps or another species. We analyzed time-resolved X-ray solution scattering (TR-XSS) results using various hypothesized mechanisms and intermediate structures, ultimately determining the mechanism that best explains the scattering signals. This mechanism initiates not from the catalyst alone, but from the complex formed between the substrate and base. Upon excitation by UVA light, the initial complex reaches an excited state. Subsequently, the aryl radical dissociates within 100 ps, forming the first intermediate. The base then reduces this first intermediate to the second intermediate, more stable intermediate with an extended lifetime. The second intermediate eventually returns to the ground state by releasing Br^-. (Figure 2) Recent studies have attempted to utilize the interactions between catalysts and other reagents. (6) However, the nature of these interactions remains elusive. Our study not only elucidates the mechanism of C-X bond activation by the catalyst, but also emphasizes the critical role of interactions between the catalyst and other chemical species in understanding the reaction.

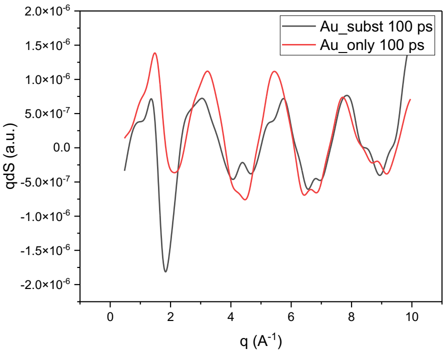

Figure 2 (Left) Difference scattering signals at 100 ps.

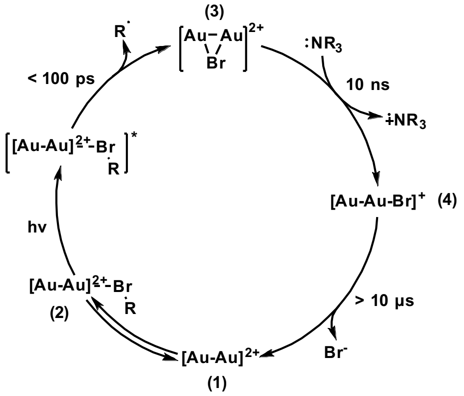

Figure 3 (Right) The suggested mechanism.

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(P-106)

Tracking the Melting Dynamics of Crystalline Ice with Time-resolved X-ray Scattering

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The melting of ice and the recrystallization of liquid water has been investigated intensively for the reason that water is one of the abundant and important substances for lives on Earth. However, the detailed mechanisms of ice melting in terms of structural dynamics were not fully elucidated despite the numerous studies using time-resolved optical spectroscopies[1,2] and molecular dynamics simulation. By combining a rapid T-jump with an intense X-ray pulse from free-electron lasers (FELs) as a probe, we could elucidate the detailed structural dynamics of ice melting. To investigate the melting and recrystallization dynamics of crystalline ice I, we conducted a time-resolved X-ray scattering experiment in the time window from ns to µs. Using information extracted from the wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) patterns, we estimated the time-dependent changes in the size and number of liquid domains, indicating that partial melting and superheating of ice occurs at around 20 ns[3]. Following that, we recently explored the earlier stages of dynamics with the wider time window (ps~us) and found interesting melting/recrystallization features on the ps and ns timescales, by analyzing the SAXS and WAXS patterns.

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(P-107)

Formation Mechanism of Alkali Halide Cluster Ion During the Electrospray Ionization: Experimental and Computational analysis

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Electrospray ionization (ESI) is a technique that converts solution samples into gaseous ions through the Coulombic explosion of sample droplets under a strong electric field. As these droplets shrink, they exhibit unique molecular behaviors distinct from bulk solution, such as the formation of unique molecular clusters and significant analyte concentration increases. However, due to the minuscule size and rapid dynamics of these nanodroplets, observing the detailed mechanisms behind these intriguing properties is challenging.

Two major ion formation mechanisms are suggested: The Ion Evaporation Model (IEM) and the Charged Residue Model (CRM). The IEM, which applies to small gaseous ions, explains ion formation as the direct ejection of ions from the charged droplet surface to alleviate excess charge. In contrast, the CRM applies to larger globular species, which ionize through the complete desolvation of surrounding solvent molecules. These processes have not been monitored directly due to their high speed and extremely small size.

To investigate these mechanisms, alkali halide clusters (M_nX_m, M=Na, K, Rb; X=Cl, I) were studied. During the ESI process, these clusters form in various sizes, and their relative intensities in the mass spectrum differ depending on the counter halide ions. This difference arises from the surface propensity of the halides: iodine prefers the droplet surface, while chloride prefers the interior. Consequently, CRM-based clusters are abundant in chlorides, and IEM-based clusters are abundant in iodides, as monitored via mass spectrometry.

Semi-empirical calculations were performed to rationalize these observations. The potential of mean force (PMF) of the clusters in droplets was calculated using gfn2-xtb. Droplet structure sampling was done using openMM simulation with the CHARMM polarizable forcefield, applying scaled-down LJ and electrostatic forces to ensure fast PMF convergence near the droplet boundary. Forces were averaged and integrated to obtain the PMF.

The results of the experiment and simulation suggest that ion formation mechanisms can be investigated by monitoring alkali halide clusters. The IEM and CRM clusters were distinguished experimentally and supported by simulation results, providing indirect evidence for ion generation mechanisms.

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Investigating the Impact of Cyclic Binders on Alkali-Halide Ionic Clusters

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Ionic clusters, formed via covalent and non-covalent interactions, are vital in electrolyte systems across various electrochemical devices. Gas-phase mass spectrometry (MS) and ion mobility spectrometry-mass spectrometry (IMS-MS) have emerged as essential tools for studying the intrinsic properties of these clusters in the absence of solvents. Integrating collision cross-section (CCS) values obtained from IMS-MS with Density Functional Theory (DFT) calculations provides insights into ion structural characteristics. Furthermore, employing Collision Induced Dissociation (CID) allows for the comparison of bond strengths between ions within clusters. This study delves into investigating how the structure and bond strength of the smallest alkali-halide ionic clusters, specifically $[M\text{-}X\text{-}M]^+$ triple ions, are impacted by cyclic binder ligands such as aza-crown ethers. Our findings demonstrate the stable dimer clusters $[L_2M_2Cl]^+$ formed by size-matched combination and the capability to control ionic bond strength through the appropriate use of binders.

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Recognition of Protein Conformation Using Iodide As Indicator Beyond Native IMS-MS

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Native IMS-MS sheds light on the quaternary structure and non-covalent interactions of protein complexes, facilitating the analysis of protein interactions in near-physiological environments. Comparison of experimental CCS values with CCS from MD simulation enables us to infer the structure of protein and their complexes indirectly, however, it is still unclear to what extent electrosprayed proteins retain their solution structure. This work demonstrates that interface-favorable iodide selectively binds to proteins maintaining their three-dimensional structure, enabling the evaluation of structural integrity in their presence. It extends beyond traditional native MS and CCS by providing additional insights into protein structure. Under native MS conditions, globular proteins displayed a narrow mass distribution corresponding to their Rayleigh charge. In line with previous study, IMS revealed one or two narrow arrival time distributions, each confirmed to the similar structure in solution though CCS values. Conversely, intrinsically disordered proteins (IDPs) exhibited broad charge distributions spanning from low to high charges. When proteins dissolved in an ammonium iodide solution were examined under identical instrumental conditions, it was observed that numerous iodide ions could bind to the globular proteins with native charge, varying depending on the protein type. However, upon the addition of HI, ubiquitin, lacking a heme group, displayed a similar iodide binding pattern to that observed with ammonium iodide. In contrast, cytochrome c and myoglobin, containing heme groups, showed few iodide binding due to acid-induced denaturation. Likewise, iodide binding was scarcely observed in intrinsically disordered proteins such as β-casein and α-synuclein. Furthermore, inducing thermal denaturation in globular proteins resulted in a decrease in the number of bound iodide ions as the structure of proteins unfolded over time. Moreover, through MD simulations, it was evident that iodide bound more effectively to folded section of protein than to unfolded section, indicating that air-water interface favorable iodide binds well when sufficient surface is formed at the protein-water interface. This study provides additional insights into the conformation of proteins beyond what could be determined solely from conventional CCS values, surpassing traditional native IMS-MS methods.

(P-110)

Flexible Plasmonic Hot-electron Photodetector using Metal-Organic Semiconductor Nanodiodes

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Plasmonic metals can convert incident light into electrical signals via localized surface plasmon resonance. The enhanced electric field generates high-energy hot electrons (1-3 eV) that can be captured and used as electrical energy when metals are bonded to oxide [1-3]. However, conventional metal-oxide nanodiodes, made with inorganic semiconductors, are fragile and easily affected by physical changes, making them unsuitable for flexible or wearable devices. In this poster, we present the demonstration of flexible plasmonic hot-electron devices that can withstand physical changes by employing organic semiconductors for the first time. The stable operation of the plasmonic $Cu/WO_3/C_{60}$ nanodiodes was verified by electrical and optical analysis. The incident-photon-to-current efficiency and photocurrent were measured under various parameters, confirming the flow of hot electrons. In addition, repeated bending and stretching up to 20,000 cycles were performed to evaluate the durability and stability of the devices as flexible photovoltaics. The results confirmed the resilience of the metal-organic semiconductor nanodiode system, indicating its ability to withstand mechanical stresses associated with flexible applications. This study holds significant importance as it expands the scope of hot-carrier devices beyond conventional rigid substrates, paving the way for their integration into flexible photovoltaics.

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(P-111)

Enhancing the photocatalytic performance of g-C_3N_4 through iron doping

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Graphitic carbon nitride (g-C_3N_4), one of the promising photocatalyst materials, is a polymer material that has a tri-s-triazine structure with C and N. It is prepared through simple thermal polymerization of N-rich materials such as melamine, urea, and dicyandiamide (DCDA). It is made from inexpensive, earth-abundant materials and has high thermal and chemical stability. It also has a band gap that allow it to absorb visible light. However, it has several serious drawbacks including the fast electron–hole recombination, narrow range visible absorption and low surface area. To overcome these drawbacks and improve the properties, much research to various modification methods of the pristine g-C_3N_4 structure.

For this reason, we doped iron which is one of transition metal into g-C_3N_4. Iron-doped g-C_3N_4 is synthesized in three different concentrations. The photocatalytic efficiencies of pristine g-C_3N_4 and g-C_3N_4 doped with iron at various concentrations are compared and confirmed through Photodegradation of methyl orange and photoelectrochemical water splitting through photoelectrodes fabrication.

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(P-112)

Synthesis of layered double hydroxide (LDH) structure using Mg and Al, fabrication of photocatalyst electrode, and photoelectrochemical analysis

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Layered double hydroxides (LDH) are inorganic layered materials composed of positively charged layers and interlayer anions with a structure similar to brucite. These materials, known as anionic clays, are combined with charge-balanced interlayer anions. LDH are synthesized for use as catalysts, catalyst supports, and host materials for nanocomposites.

Layered double hydroxides are ionic solids with a layered structure composed of octahedral units, consisting of positively charged metal hydroxide layers and interlayer anions. The interlayer anions are weakly bound, allowing for the exchange of these anions with various others. Similar skeletal structures can be constructed with different combinations of divalent and trivalent metals, resulting in diverse chemical properties. In this study, LDH structures were fabricated using Mg and Al, and their electrochemical properties were evaluated by utilizing these materials as photoelectrodes.

To find the optimal conditions for fabricating MgAl-LDH photoelectrodes, MgAl-LDH was synthesized using the co-precipitation method, and then the MgAl-LDH solution was deposited onto an FTO substrate using spin coating. Various parameters, such as the spin coating RPM and the content of divalent and trivalent cations in the deposition solution, were adjusted to produce the electrodes. The surface morphology and chemical composition of the MgAl-LDH electrodes were analyzed by SEM and EDS, respectively. The structural characteristics of MgAl-LDH were determined by XRD analysis, and the photocatalytic and electrochemical properties of the MgAl-LDH electrodes were analyzed using LSV and CA.

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(P-113)

Hydrogen Evolution Reaction of WC-Based Catalyst

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Hydrogen is gaining significant attention as an eco-friendly and renewable energy source, with extensive research being conducted on its production. However, the commercialization of hydrogen energy faces challenges due to its economic infeasibility. Among the methods for hydrogen production, the electrochemical water splitting process presents economic issues such as high energy consumption and efficiency reduction due to elevated overvoltages. Various materials are being explored to mitigate these issues and enhance the catalytic activity of the hydrogen evolution reaction (HER). Noble metals like Pt, Ir, Rh, and Ru demonstrate superior catalytic properties and low overpotential but are not viable for mass production due to their high cost.

Consequently, non-precious metal catalysts are emerging as an efficient and practical substitute for large-scale production. In this regard, transition metal carbides (TMCs), with their high electrical conductivity and d-band electron density states akin to Pt, are showing promise. Specifically, WC has exhibited catalytic behavior for HER comparable to Pt.

This study focuses on depositing Ni-WC and NiCo-WC catalysts to minimize overpotentials associated with HER, enhance catalytic activity, and offer a more cost-effective solution. The structural properties of the fabricated electrode were analyzed using X-ray Diffraction (XRD). Surface and compositional analyses were conducted using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).

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(P-114)

Enhancing Photoelectrochemical Oxidation of 5-Hydroxymethylfurfural to 2,5-Furan Dicarboxylic Acid Using $BiVO_4$ with Improved Charge Transfer Mediators

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While the momentum of COVID-19 has slowed in recent years, the aftermath has not yet subsided. One of the most serious problems is the increased amount of plastic waste caused by the impact of COVID-19. A noticeable percentage of plastic waste is polyethylene terephthalate (PET), a petroleum-derived plastic that takes over 150 years to decompose. However, these problems can be solved by using polyethylene furan dicarboxylate (PEF) derived from biomass. Unlike PET, PEF takes only 40 years to decompose, minimizes carbon dioxide emissions, and has the advantage of preventing environmental pollution because it decomposes well when buried in soil.

PEF can be obtained by the polymerization of 2,5-furan dicarboxylic acid (FDCA) and ethylene glycol (EG). FDCA can be obtained by oxidizing 5-hydroxymethylfurfural (HMF). HMF is a substance obtained from glucose through isomerization and dehydration, and it has been in the spotlight so far because it can be converted into various value-added chemicals. Because of these advantages, studies on the oxidation of HMF to FDCA are being actively conducted. There are several methods for oxidizing HMF to FDCA. Among them, the electrochemical oxidation of HMF to FDCA proceeds in a milder environment compared to using a heterogeneous catalyst. Among electrochemical oxidation reactions, photoelectrochemical oxidation has recently been actively studied due to its advantages of being environmentally friendly and utilizing the sun.

Among several photocatalysts, $BiVO_4$ has attracted significant attention due to its moderate bandgap, low toxicity, and relatively low cost. However, it is difficult to use $BiVO_4$ in practical applications due to disadvantages such as poor electron transfer ability and recombination, which is the process where electrons that move to the conduction band recombine with holes. Here, a charge transfer mediator was easily deposited to improve the low electron transfer ability, which is one of the disadvantages of $BiVO_4$ material. As a result, better PEC efficiency and HMF oxidation conversion rates were confirmed compared to pure $BiVO_4$.

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(P-115)

High-level theory for (photo)(electro)chemical interfaces

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Chemical reactions are fundamentally essential across all scientific fields. For these reactions to occur, reactants and reaction environments are necessary, and consequently, a homogeneity of reactants or environments can form at the interface. In such situations, external stimulations, such as light or electricity, are often applied to accelerate or suppress chemical reactions at the interface [1-3]. Furthermore, solvation can be inevitable; otherwise, the observation or detection may not be feasible due to stability issues or sluggish kinetics [4]. Thus, to observe or understand these chemical reactions at the (photo)(electro)chemical interface as a stage for the reactions, unlocking the intrinsic properties of the interfaces needs to be prioritized. However, a well-established theory has not yet been formulated due to the intrinsic interfacial complexity or the resolution limit, either experimentally or theoretically.

To address this issue, we developed a new methodology based on many-body perturbation theories to understand the optoelectronic properties of chemical systems in solutions, which closely aligns with experimental observations of their electronic structures, including the positions of band edges. Additionally, we have defined the relationship between the structure and properties of porous systems. Our theory also accurately predicts experimental optical properties, such as the solvatochromic effect as well as excitonic behaviors. Thus, this theoretical method serves as an efficient theory to elucidate a wide range of chemical reactions at photoelectrochemical interfaces.

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(P-116)

Chiral Recognition of Amino Acid, Ephedrine, and Pseudoephedrine Combined with β-cyclodextrin Using Cryogenic Ion Trap Spectroscopy

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The chirality of amino acids and chiral molecules was distinguished using the permethylated β-cyclodextrin complex. We obtained the UV photodissociation(UVPD) of N_2 tagged permethylated β-cyclodextrin/H^+ephedrine, pseudoephedrine, and amino acids complexes ions produced by electrospray ionization and stored in a cryogenic ion trap near the origin band of the S_0-S_1 transition. The spectrum of each enantiomer of pseudoephedrine and amino acids complexes showed different spectra, but each enantiomer of ephedrine complexes showed similar spectra. IRPD spectra were also obtained in the same way as UVPD and experiments were conducted on ephedrine and pseudoephedrine. Two enantiomers of pseudoephedrine complexes appeared with different spectra but enantiomers of ephedrine complexes looked very similar to each other. So we can distinguish whether both chiral centers are R or S configurations. However, it was confirmed that if each chiral center had a different configuration, it could not be distinguished. The IR spectrum will be assigned with the theoretical calculation results.

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NIR Photoluminescence Enhancement of Ag_2S Nanoparticle by Chloride Passivation

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Silver sulfide (Ag_2S) nanocrystals have gained scientific attention in recent years based on their unique optical and electronic properties. Ag_2S nanocrystals possess a narrow band-gap semiconducting materials (a band-gap for bulk Ag_2S is ~ 1.1 eV), which allows that they can show photoluminescence in the short-wave infrared (SWIR) region, 900~1700 nm with a significant absorption cross section.[1] Furthermore, because of their non-toxic and environmental-benign elemental compositions without cadmiums and leads, they have large possibilities for practical applications for NIR-active materials.[2]

On a basis of these advantages, we studied NIR photoluminescence and electronic properties of Ag_2S nanocrystals. Here, we focused on the rich Ag-terminated Ag_2S nanoparticles due to their facile preparation and surface modification arising from their two kinds of surface ligand, octylammonium and nitrate.[3,4] With a simple sonication treatment under a chloric-solvent environment, $CHCl_3$, we verified that ligand exchange from alkyl amine to chloride results in an effective passivation and enhancement of NIR photoluminescence which is intensively investigated with NIR steady-state fluorescence and time-corelated single photon counting measurements.

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(P-118)

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, its triplet ground state and strong O-O bond make direct reactions between dioxygen and singlet organic substrates 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. Unlike these metals, aerobic nickel-based oxidation chemistry in nature is limited to a 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 been shown to be useful for reducing O_2. Thus, we have chosen organonickel complexes, $(bpy)Ni^{II}(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ and $(py_3CH)Ni^{II}(CH_2CMe_2\text{-}o\text{-}C_6H_4)$, 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 from Ni^{II} with bpy ligand and a monomeric Ni intermediate from Ni^{II} with py_3CH ligand could be defined.

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Unveiling the High-Resolution Structures of Aromatic Molecule-Iodine Atomic Complexes with 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 uncover the dynamic structure of aromatic molecules-iodine atomic charge transfer complexes using time-resolved X-ray solution scattering.

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(P-120)

Excited-state Reductive Elimination Reactions of Low-valent Acyclic Organonickel Complexes

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For conventional bond-forming reductive elimination (RE) reactions in Ni(II)-catalyzed cross-coupling reactions, high-temperature conditions or prolonged reaction times are typically required. The energy transfer via photocatalysts or direct photoexcitation has emerged as a method to accelerate the rate-determining RE reactions of organonickel(II) complexes. We have investigated the excited-state carbon-carbon bond-forming RE activities of acyclic Ni(II) species with $(Me)_2$, $(Mes)_2$ and (Mes)(Me) substrates. While the nickelacycle with cyclonephyl substrate did not show the excited-state activity[1], excited-state acyclic Ni species generated C-C coupled products. Upon direct photoexcitation, Ni(II)$(Me)_2$ generated a mixture of ethane and methane. This result is consistent with our previous research indicating that direct photoexcitation can induce Ni-C bond homolysis through the ^{1}dd transition followed by intersystem crossing to the ^{3}LMCT state. However, Ni(II)(Mes)(Me) and Ni(II)$(Mes)_2$ exhibit nearly 100 % yields of their repective C-C coupled products, Mes-Me and Mes-Mes. To understand this excited-state reactivity of RE, the electronic structures of excited-state Ni intermediates have been investigated by electron paramagnetic resonance spectroscopies and density functional theory computations.

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(P-121)

Twisted Intramolecular Charge Transfer of Anthraquinone Derivatives Confined in *methanol-in-oil* Reverse Micelles

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Excited-state intramolecular charge transfer (ICT) has been extensively studied experimentally and theoretically due to its applications to solar energy conversion, photovoltaics, fluorescence sensing, etc. [1] Recently, femtosecond stimulated Raman spectroscopy results for the ICT dynamics of 1-aminoanthraquinone (1AAQ) showed an ultrafast (110 fs) ICT dynamics with the internal rotation of the amino group, where the major vibrational modes of $\nu_{C\text{-}N} + \delta_{CH}$ at 1200-1230 cm^{-1} and $\nu_{C=O}$ at 1300-1330 cm^{-1} represent the structural changes of 1AAQ upon ICT. The ICT dynamics of 1AAQ also varies the vibrational modes of surrounding DMSO solvents, where the hydrogen bonding network of DMSO was changed during the excited-state dynamics of 1AAQ. [2]

In this research, the ICT dynamics of 1AAQ and its derivatives, 2-aminoantharquinone (2AAQ), and 1-methylaminoanthraquinone (1MAAQ) are investigated using femtosecond transient absorption and fluorescence upconversion spectroscopy in *methanol-in-oil* Igepal reverse micelles (RMs). The decreased ICT dynamics of AAQ derivatives in RMs show a strong correlation with the structural difference of functional groups attached on anthraquinone backbone. This can be understood as the different rotational dynamics of amino or methylamino group with the increase in microviscosity inside the nanopools of RMs. Additionally, the ICT dynamics of AAQ derivatives in aliphatic alcohols are also measured to estimate the microviscosities inside the *methanol-in-oil* Igepal RMs, and show lower microviscosities values reported for the *water-in-oil* AOT RMs [3] which might be related to the reduced hydrogen bonding of methanol cores than water cores and negligible surfactant charges of nonionic Igepal surfactant.

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(P-122)

Chiral Discrimination of Common Monosaccharides by Surface-Enhanced Raman Spectroscopy

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Chiral discrimination of biomolecules has gained significant attention across various fields such as pharmacology, biochemistry, *etc.* due to the crucial role of chiral-selective molecular interactions in many biological pathways within living organisms [1]. Circular dichroism (CD) has traditionally been utilized as a chiroptical method for chiral discrimination, but limited sensitivity and insufficient molecule-level information have constrained its widespread application. Surface-enhanced Raman scattering (SERS) has emerged as a promising alternative to CD due to its capability to provide molecular fingerprint information with high sensitivity. The chirality of analytes can be distinguished from the changes in the SERS spectra of reporters by the chiral-selective intermolecular interactions between the reporters and analytes [2]. Nevertheless, most previous reports on chiral discrimination by SERS have lacked a comprehensive understanding of the chiral-sensitive changes in the surface adsorption and SERS spectra of both chiral reporters and analytes at the molecule-level.

In this study, the chiral detection of common monosaccharides was investigated by SERS spectral changes of a chiral reporter, phenylalanine (Phe) adsorbed on gold colloidal nanoparticles (AuNPs). The SERS of Phe was drastically changed only when monosaccharides of the same chirality as Phe were added to Phe-AuNPs mixtures. In addition, the SERS spectral changes of Phe were observed to vary depending on the type of added monosaccharides. For example, with the addition of glucose (Glu) or mannose (Man) of matching chirality, the increase of $\delta(COO^-)$ and the decrease of $\nu_s(COO^-)$ in the SERS of Phe were observed, indicating a change in the surface adsorption of Phe through the carboxylate from bidentate to monodentate binding on the AuNPs [3]. On the other hand, upon adding Fru of matching chirality, the increases of lower-symmetry phenyl ring vibrations and $\delta(NH_2)$ + $\delta(CH/CH_2)$, and the disappearance of $\delta(COO^-)$ were observed, suggesting the adsorption geometry change of Phe via the carboxylate to bidentate binding with closer proximity of phenyl ring, amine, and aliphatic CH/CH_2 groups to the AuNP surface. Based on the chiral-sensitive SERS of Phe, the quantitative analysis of the monosaccharide concentration was performed. The intensity ratios of the SERS bands of Phe to invariant ν_{12} or ν_{8a} modes showed linear correlations with the concentrations of monosaccharides of matching chirality in the range of 2×10^{-5} to 2×10^{-9} M and 2×10^{-5} to 2×10^{-7} M in the absence and presence of monosaccharides with opposite chirality, respectively.

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(P-123)

Intramolecular Charge Transfer of Stilbazolium Derivatives investigated by Femtosecond time-resolved Spectroscopy

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Chromophores where electron donor and acceptor moiety are connected by skeletal π-bridge structure often shows internal structural changes of backbone, such as the rotation of donor or acceptor group. Intramolecular charge transfer (ICT) is one of the fundamental chemical processes where the charge transfers occur between the electron donor and acceptor groups. Many researchers have recently investigated the ICT dynamics of chromophores including π-bridge and suggest that structural changes of electron donor or acceptor moiety occur upon the photo-induced excited state with time-resolved electronic probes and theoretical calculation results by time-dependent density function theory(TDDFT). Since the electronic spectroscopy is fundamentally not sensitive to these structural changes, detailed experimental evidence for the twisted motion in the ICT dynamics have rarely been reported and time-resolved vibrational spectroscopy such as femtosecond time-resolved Raman spectroscopy (FSRS) is required to reveal the internal structural changes of chromophores(*1*). In this work, *para-* and *ortho-* 4-N,N-diethylamino-N'-methylstilbazolium tosylate (DEST) isomers are selected to understand the effect of steric hindrance at the pyridium moiety upon the ICT dynamics. The two isomers of DEST appear quite similar in transient absorption (TA) measurements, which shows that both isomers show apparent ICT dynamics in the excited states. However, further information about the structural changes accompanying the ICT process, such as the rotation of electron donor or acceptor moiety, should be needed from the TA measurements. Therefore, structural changes of similar 4-N,N-diethylamino-4"-N'-methylstilbazolium tosylate (DEST) derivatives will be discussed with skeletal vibrational modes (ν_8) and π-backbone decoupling by FSRS. FSRS results of DEST isomer clearly shows vibrational mode coupling of diethyl-aminophenyl and pyridium group at the ground state of both isomer although new isolated ν_{8a} (ph) mode at the ~ 1650 cm^{-1} only appears at the *para*-isomer with the strongly blue-frequency shift and kinetics of ICT states (~ 4 ps). Furthermore, previously reported Raman band of *p*-DEST at the excited state is separated due to the improvement of spectral resolution of FSRS setup. The skeletal vibrational modes of styrylpyridinium backbone and similar geometry cases are suggested as one of the sensitive experimental probes for the structural changes in the ICT dynamics(*2*).

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Photo-induced carbon–sulfur cross-coupling reactions of organocobalt(III) complexes and its mechanistic understanding

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Cobalt catalysts are one of prominent early transition metal system that facilitates the cross-coupling reactions, particularly for carbon–carbon cross-coupling reactions. [1] Despite extensive investigations into carbon-carbon cross-coupling reactions, research on cobalt-catalyzed carbon-heteroatom cross-coupling reactions remains relatively sparse. The current understanding of the cobalt-catalyzed cross-coupling reactions are also limited, organocobalt complexes are reported as intermediate in the catalytic cycle. [2] To address the research needs in cobalt-catalyzed cross-coupling reactions, four distinct alkyl sulfide-ligated organocobalt(III) complexes were synthesized. The cross-coupling reactions of these complexes were induced by either heating or irradiation of light, and the effects of these energy sources on the reactions were investigated. The reactivity of organocobalt(III) complexes differed between ground state reactions in the dark environment and excited state induced reactions, suggesting distinct reaction pathways for ground state and excited state reactions. Notably, carbon-sulfur (C–S) cross-coupling reactions were initiated upon irradiation of the sulfide-ligated organocobalt complexes, whereas no C–S cross-coupling products were observed from the ground state reactions. To elucidate the mechanism of the excited state mediated pathways, various methodologies were employed, including low-temperature NMR spectroscopy, kinetic studies, product and intermediate characterization by EPR spectroscopy, and the impact of radical scavengers on reactivity.

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(P-125)

Dioxygen reaction of an organonickel(III) complex

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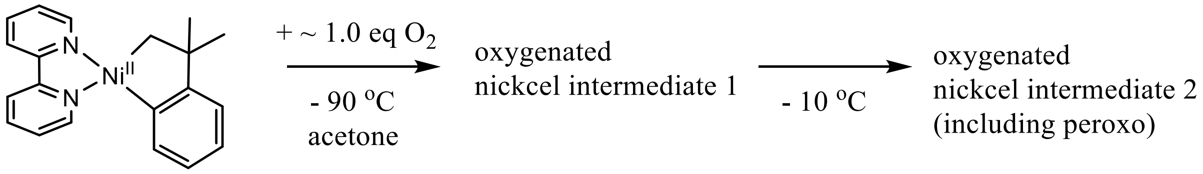
Metalloenzymes enable various redox reactions that are challenging to achieve for organic molecules alone. Enzymes that react with O_2, environment-friendly oxidants abundant in nature, have been extensively studied. To study O_2 reactions, many scientists have developed biomimetic systems that mostly contain iron or manganese. Using nickel for O_2 activation is a difficult task due to its relatively high effective nuclear charge. Our group has confirmed that both divalent and trivalent organonickel complexes can perform O_2 activation. Given the fact that generally trivalent nickel centers do not have reducing power strong enough to activate dioxygen, our results imply that carbon-based ligands can donate electron density significantly to the metal center, resulting in a highly covalent nature for Ni(III)-C bonds. To elucidate correlations between the electronic structure and O_2 reactivity of Ni(III)(bipyridine)($CH_2C(CH_3)_2$-*o*-C_6H_4),we have utilized various spectroscopies such as electronic absorption, ^1H NMR, and resonance Raman spectroscopies and characterized the reaction species including oxygenated intermediates. A peroxo-level intermediate was first detected from trivalent organonickel O_2 reaction, and its reactivity with the carbon ligand and other exogenous substrates have been examined. We anticipate that this mechanistic understanding will provide key insights into the design of O_2 utilization for organonickel reactions and the nature and reactivity of Ni-C bonds at high-valent oxidation states.



SCHEME 1. O_2 reaction of Ni(III)(bipyridine)($CH_2C(CH_3)_2$-*o*-C_6H_4)

(P-126)

First-Principles Calculations of Direct and Indirect Auger Recombination Coefficients in $In_xGa_{(1-x)}N$

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Recently, indium gallium nitride (InGaN) based micro-LEDs (μLEDs) have gained significant attention due to their potential uses in next-generation high-performance displays. The μLED display technology needs distinct red, green, and blue (RGB) μLEDs as a single pixel for full-color displays. Currently, InGaN materials are used to make blue and green μLEDs, whereas normal-sized aluminum gallium indium phosphide (AlGaInP) is used to make red LED chips. However, when the chip size of AlGaInP LEDs is reduced to micro size, the efficiency drops down dramatically due to high surface recombination and long carrier diffusion lengths.[1] Therefore, extending the emission wavelength of InGaN-based LEDs from blue/green to red is the optimum choice to replace AlGaInP red μLEDs for micro-displays. However, to achieve red emission, the In-content in the quantum wells (QWs) must be more than 30%, which significantly lowers the internal quantum efficiency (IQE) of the μLED.[2] The IQE of InGaN materials across a broad wavelength of the spectrum is limited by defects, carrier leakage, poor hole injection, and Auger recombination. At high current densities, Auger recombination becomes a significant nonradiative loss process as it scales with the cubic power of the free-carrier concentration.[3,4] In this work, we evaluate the direct and indirect Auger recombination coefficients for electron-electron-hole (*eeh*) and hole-hole-electron (*hhe*) recombination processes in a series of $In_xGa_{1-x}N$ (x = 0-0.42) materials by using density functional theory (DFT). We demonstrate that the phonon-assisted indirect Auger processes are more prevalent in GaN than the direct Auger recombination. We find that InGaN alloys exhibit a greater dominance of both direct and indirect Auger processes in comparison to GaN. More importantly, we observe that both the direct and indirect Auger coefficients increase with the increasing In-contents and thus will reduce the IQE. At room temperature, the calculated Auger coefficients of InGaN alloys can be as large as 5.53×10^{-31} cm^6s^{-1}.

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(P-127)

Conformational Exploration Using Neural Network Potential: Training Dataset Generation Based on H-bond Patterns

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A neural network potential (NNP) model using the SchNetPack architecture[1] was trained to explore the conformational space of a singly protonated hexapeptide, DYYVVR. Structural identification by matching simulated vibrational frequencies with experimental spectra is limited for small-sized system if the system contains highly correlated vibrational modes. Its conformational diversity increasing exponentially with the system size also makes such research even harder. To mitigate such size problems, we applied a fragmentation approach to reduce computational cost and trained NNP models with DFT data of capped fragment structures and small number of parent structures. In order that trained models predict energies and forces of various conformational isomers properly, training data should contain various atomic environments as much as possible. To make a dataset of parent structures that covers broad conformational space, we classified structures based on the H-bond patterns and selected structures so that the dataset has all types of H-bonds in the system. As a result, we were able to train the model for DYYVVR with mean absolute errors of 5.08 kJ/mol for energy and 2.24 kJ/molÅ for force compared with DFT computed values at the M06-2X/6-311+G(d,p) level of theory. Further optimizations of the model are in progress to make a standard operating procedure and we are planning to enlarge its applicability.

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(P-128)

In Situ Temperature Measuring Cathodoluminescence in Transmission Electron Microscopy

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Transmission electron microscopy (TEM) is a powerful technique for examining materials at the atomic scale, providing unprecedented insights into their structural details. Recent advancements have extended beyond improving spatial resolution to include *in situ* characterization under various external stimuli, such as electrical bias,[1] mechanical force,[2] and laser irradiation.[3] These stimuli may also induce localized temperature change in a TEM sample, but temperature determination has been challenging technically and in precision.[4]

Here, we report *in situ* nanothermometry in TEM utilizing cathodoluminescence (CL) from europium-doped (Eu^{3+}) gadolinium oxide.[5] The nonradiative transition among the excited states of Eu^{3+} follows temperature-dependent multi-phonon relaxation, thereby affecting relative CL intensities of the transitions. The CL-intensity ratio of the transitions from different excited states serves, therefore, as a thermometric parameter, achieving the precision of ±5 K within a temperature range of 113-323 K. With the CL-based thermometry, we further demonstrate measuring local temperature under laser irradiation.

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(P-129)

Particle-Specific Thermally-Induced Phase Transition of Freestanding Polycrystalline Vanadium Dioxide

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Vanadium dioxide (VO_2) was discovered to exhibit structural phase transitions (SPT) and insulator-metal transitions in 1959.[1] VO_2 was known to undergo SPT from a high-temperature metallic rutile (R) structure to a low-temperature insulating monoclinic (M1) structure. The SPT of VO_2 occurs at a low SPT temperature ($T_c \approx 67$ °C) and can be driven by intense optical or electrostatic fields, and heating. Various theories, such as Mott-Hubbard and Peierls, have been proposed to investigate the correlation between electronic and lattice degrees of freedom.[2] However, the debate over the transition mechanism remains unresolved. The various structural properties of VO_2 particles can induce different optical and electrical characteristics,[3] but tracking the structure-property correlations is formidable from the studies based on the measurements on ensembled samples. This calls for imaging that can film the evolution of structural parameters of each particle in space.[4]

In TEM images, diffraction contrast is highly sensitive to crystallographic changes within intraparticle and strain field distributions, the change of which provides a direct measure of structural transitions. Cross-correlation of diffraction contrast shows differences in the width of the hysteresis loop and SPT temperature among individual nanoparticles. The analysis of differences in SPT properties among nanoparticles is formidable in ensemble measurements within electron diffraction or optical spectroscopy. This study suggests the potential of observing and mapping the transitions of all nanoparticles in the imaging area.

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(P-130)

Laser Induced Self-Assembly of Proteins Using *In-Situ* CryoTEM

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The microtubule (MT) is a well-known cytoskeleton component with a hollow cylinder-like filament architecture. The major component of MT is a heterodimer of two tubulin subunits: α- and β- tubulins. It plays pivotal roles in a wide range of eukaryotic cellular processes crucial for cell function and viability, for example, maintaining cellular shape and structural integrity, serving as tracks for intracellular transport and cell division.[1] In the cell division process, MTs organize into a mitotic spindle during mitosis (or meiosis), ensuring the accurate segregation of chromosomes into daughter cells. The dynamic instability of microtubules, characterized by rapid switching between phases of growth and shrinkage, allows them to respond quickly to cellular signals and adapt to changing intracellular conditions. Regulation of microtubule dynamics operates through various mechanisms, including the availability of tubulin subunits, the presence of microtubule-associated proteins, and post-translational modifications of tubulin proteins. Disruption of microtubule dynamics affects significantly on cellular function and viability, making them important targets for therapeutic intervention in diseases such as cancer, where agents that modulate MT dynamics are utilized to inhibit cell division and induce apoptosis in cancer cells.[1,2]

Here, we directly monitor the appearance of MTs from tubulin subunits that are embedded in the vitreous ice layer by utilizing cryogenic transmission electron microscopy (CryoTEM). Electron microscopy has been vigorously dedicated to numerous MT-related studies. However, all the previous studies have delivered static images of MT filaments.[3] *In situ* TEM allows us to investigate biological systems in real time on the timescale of sub-second. Here, we integrate the light-coupled *in situ* TEM to CryoTEM to visualize the formation of MT assembly under the irradiation of femtosecond laser pulses. To suppress the dynamic instability, *i.e.*, the deformation of MT, a famous MT-target anticancer drug, paclitaxel (Taxol), was treated with a tubulin cocktail. Bright-field images of MTs after the laser irradiation were investigated, together with the crystallized water, which was formed concomitantly with MTs. It was found that local transient heating by laser irradiation is the driving force for forming MT filaments. Based on the results, we successfully demonstrated a powerful *in situ* imaging for the biological architectures in vitreous ice to track biological dynamics.

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(P-131)

Stepwise Termolecular Acid-Base Reaction: Spectrally and Kinetically Captured Eigen Complexes

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In the Eigen–Weller model,[1,2] acid-base reactions are characterized by a sequence of steps: encounter between acid and base compounds via diffusion, short-range proton transfer within the encounter complex, and dissociation of the resulting Eigen complex (EC), which corresponds to long-range proton diffusion. While substantial research has focused on the initial proton transfer within the encounter complexes,[3] unfortunately, the final step necessary for terminating the acid-base reactions has been discounted.[4] Here, based on time-resolved fluorescence spectroscopy and chemical-kinetics analysis, we monitor the excited-state proton transfer of a cationic photoacid, *N*-methyl-7-hydroxyquinolinium, to an aprotic base, dimethyl sulfoxide (DMSO), in acetonitrile.[5] By identifying the EC both spectrally and kinetically, we examine the molecularity of consecutive steps in the Eigen–Weller framework: hydrogen-bond formation between the acid and base and the dissociation of the EC. We reveal that two DMSO molecules cooperate to dissociate the EC and stabilize the dissociated proton in a quasi-Zundel configuration, terminating the model acid-base reaction.[6]

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(P-132)

Global-Analysis Simulation of a Reversible Two-State Kinetic Model for Excited-State Dynamics

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Elucidating chemical kinetics is essential for understanding the mechanisms of chemical and biological reactions. In this regard, excited-state proton transfer (ESPT) has been studied as a platform for investigating the mechanisms in acid-base reactions. Many experiments have been conducted tracking how the populations of reactants and products in the excited state (ES) change in time with reaction conditions such as temperature, the concentration of acid or base, and solvent properties. The simplest reaction would involve only two species in ES: a reactant and a product. However, in the two-state ES model, even without a reverse reaction, the associated chemical kinetics has not been meticulously considered; in some cases, the sign reversal of the pre-exponential factor for the bi-exponential fluorescence profile of the product has been puzzling.[1-4] With the reverse reaction in ES, elucidating the chemical kinetics becomes more complicated. Here, we analytically solve differential rate equations for the reversible two-state model to obtain time-dependent concentration of each species in ES. With the solutions, we show how the global lifetimes and their lifetime-associated spectra change with the various combinations of rate constants. The simulation results are compared to experimental results on ESPT for demonstrating the validity of the solutions.[5] The presented global-analysis simulation is applicable to any two-state reactions in ES.

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(P-133)

Quantification of the Hydrogen-Bonded Formation of a Super-Photoacid in Aprotic Solvents by Time-Resolved Spectroscopy and Scrutiny of its Excited-State Dynamics

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Identifying and quantifying hydrogen (H)-bonded complexes is pre-requisite to studying the reaction mechanism of proton transfer. The Benesi-Hildebrand method has traditionally been used to determine the formation constants of H-bonded complexes, assuming that H-bonding additives only cause spectral change exclusively through the H-bond formation.[1,2] However, if the introduction of the additive affects the bulk polarity of the solution, accompanying a spectral shift, the Benesi-Hildebrand method becomes compromised. In this study, we investigate the H-bond formation between a model cationic photoacid and a weak organic base of dimethyl sulfoxide in an aprotic medium. We quantified the fractions of two coexisting pathways involved in the excited-state proton transfer (ESPT) of a super-photoacid: the ultrafast ESPT of the H-bonded complex and the diffusion-controlled ESPT of the free photoacid. Our approach surpasses the accuracy of conventional steady-state spectroscopic approaches by directly quantifying the H-bonded complexes through the chemical-kinetics analysis, thereby bypassing the aforementioned limitation.[3]

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(P-134)

Proton-Transfer Dynamics of a Photoacid with Water in a Diffusion-Controlled Regime

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Proton transfer is an important reaction prevalent in many chemical and biological processes. Understanding the mechanism of the proton transfer with water molecules is essential in understanding acid-base reactions in aqueous solutions and various metabolic processes in organisms. Here, we study the proton transfer of *N*-methyl-7-hydroxyquinolium ($NM7HQ^+$), which is a photoacid, to water acting as a base in an inert solvent of acetonitrile by inspecting the time-resolved spectral evolution of the photoacid. The reaction was initiated by photoexcitation to form an encounter complex between the photoacid and the base via forming a hydrogen (H) bond.[1] Through the steady-state absorption-spectral analysis, we confirmed the formation of a H-bonded complex in the ground state. For tracking excited-state dynamics, fluorescence kinetic profiles were measured using the time-correlated single photon counting spectroscopy. The temporal behavior of the fluorescence of $NM7HQ^+$ was analyzed based on the Eigen-Weller model. Three different lifetime components were unveiled capturing an intermediate species in the course of the excited-state proton transfer. By solving rate-law equations analytically, we were able to evaluate the rate constants of each consecutive step and determine the molecularity of water involved. Based on the findings, we propose the full reaction mechanism.

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(P-135)

Cryogenic Ion Spectroscopy of an Insulin Receptor Peptide and Development of a Home-made Ion Spectroscopy Mass Spectrometer

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Regulation of the kinase activity of the insulin receptor is influenced by phosphorylation of its three tyrosine residues (Tyr1146, Tyr1150, and Tyr1151) located in the kinase activation loop. Phosphorylation state of a peptide can be studied by UV ion spectroscopy. [1,2] We performed cryogenic ion spectroscopy (CIS) of singly protonated DIYETDYYR, a tryptic peptide of the insulin receptor containing the active three tyrosine residues and its point mutants [(Y1146F, Y1150F), (Y1150F, Y1151F) and (Y1146F, Y1151F)]. Though it was possible to observe ultraviolet photodissociation (UVPD) of the peptides at room temperature, the size of the peptide was too large to observe good dissociation yield in the cryogenic UVPD experiment. However, significant spectral differences between the peptides were observed in the cryogenic H_2-tagged infrared photodissociation (IRPD) experiment. We upgraded our existing room-temperature ion spectroscopy mass spectrometer to enable cryogenic spectroscopy experiments by equipping it with a closed cycle helium cryostat. Cryogenic UVPD of tyrosine and single protonated DIYETDYYR can be performed using the upgraded cryogenic spectroscopy mass spectrometer. In order to enhance UVPD yield at cryogenic temperature, UV-1064-PD experiments and H_2O tagging UVPD experiments are planned.

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(P-136)

Solvent- and Pump-Fluence-Dependent Exciton Dynamics in One-Dimensional Perylene Bisimide H-Aggregates

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Supramolecular dye assemblies, particularly those formed by perylene bisimide dyes, hold tremendous potential for applications in optoelectronics. Thus, understanding the complex exciton dynamics within these assemblies, especially in H-type aggregates which can be a good candidate for light-harvesting application due to the generation of long-lived excitons, considered critical in photochemistry. In this study, we investigate the comprehensive dynamics of delocalized Frenkel exciton, localized excimer and charge separation of π-π stacked perylene bisimide aggregates. Through analysis of femtosecond and nanosecond transient absorption spectra, we demonstrate that in helical π-stacked aggregates, the initial delocalized Frenkel exciton go through charge separation process within few picoseconds and undergoes relaxation pathways, such as charge recombination process within tens of picoseconds. Also, we revealed the existence of exciton-exciton annihilation (EEA) channel in long axis of helical aggregates through pump fluence dependence transient absorption experiments. We figured out EEA process take place within hundreds of femtoseconds before the charge separation process occurs, so the EEA process can affect the processes that follow. Our experimental findings reveal novel insights into the delocalized Frenkel exciton dynamics and exciton annihilation channel in helical π–π stacks of perylene bisimide dyes. This study contributes to the ultrafast exciton dynamics of molecular H-aggregates, crucial for advancing material performance in various applications, and underscores the importance of understanding exciton behavior in dye self-assemblies.

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(P-137)

Coexistence of Conformational Isomers Displaying Distinct Excited Dynamics and Exciton Coupling in Diphenylanthracene Dimer

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9,9-Bianthracene (BA) is a prominent material for studying Symmetry-Breaking Charge Transfer (SBCT) due to its structural simplicity and controlled torsional SBCT mechanism. Its orthogonal structure typically results in a mono-exponential fluorescence decay, highlighting the uniformity of its conformers. Recently, the exploration of bianthracene derivatives like 2,9’-Bianthracene and 1,9’-Bianthracene has not yielded significant deviations from BA's properties, primarily because of their similar orthogonal structures. Here, this study introduces 9,9’,10,10’-Tetraphenyl-2,2’-bianthracene (TPBA), exhibiting a markedly different geometric structure and excited-state dynamics compared to BA. The reduced steric hindrance in TPBA facilitates a tendency towards planarity, enhancing short-range exciton coupling and leading to an adiabatic mixing of locally excited (LE) and charge transfer states (CT). Quantum mechanical calculations have revealed two distinct local energy minima in TPBA, characterized by dihedral angles of 35° and 141°, corresponding to trans and cis conformers with different energy levels. Utilizing time-resolved fluorescence spectroscopy with an iCCD camera, we identified differing emissive spectra and decay kinetics for these conformers, specifically 5 ns for trans and 30 ns for cis with maximum at 500 nm and 425 nm. Further analysis showed that the trans conformer exhibits a higher radiative (6.98×10^7 s^{-1}) and non-radiative rate (13.0×10^7 s^{-1}) compared to the cis conformer, which displayed slower rates (radiative: 0.532×10^7 s^{-1}, non-radiative: 2.86×10^7 s^{-1}). These differences are supported by time-dependent density functional theory (TD-DFT) calculations, highlighting a fourfold greater oscillator strength for the (0,0) transition in the trans conformer. Additionally, potential energy surface scans and geometry optimizations based on DFT/TD-DFT revealed a higher torsional barrier in the excited state of the cis conformer, limiting its torsional freedom and resulting in a decreased non-radiative decay rate. Our findings highlight the significant impact of linkage positions on the photophysical behaviors of trans and cis conformers, contributing valuable insights towards the advancement of optoelectronic device technologies.

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(P-138)

The Impact of Oligothiophene Linkers in Heterogeneous Triplet Formation Pathways of 6,6'-Linked Pentacene Dimers

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Singlet Fission (SF), a phenomenon where one singlet exciton generates two triplet excitons, is exclusive to organic semiconducting materials[1]. This phenomenon has been attracting considerable attention due to its potential to exceed the Shockley-Queisser limit through carrier multiplication in photovoltaics[2,3]. A molecular dimer covalently bonded serves as the basic model for understanding SF mechanisms because it consists of two closely interacting chromophores, thus capable of yielding two excitons[4]. In this research, we explored the intramolecular SF dynamics of pentacene dimers linked by 6,6'-connections with various oligothiophene linkers to elucidate the role of linkers in controlling SF pathways. Through femtosecond transient absorption (TA) measurements, we found that SF behaviors are heavily influenced by the number of oligothiophenes in the linker and the presence of ring fusion. Furthermore, we selectively excited specific conformers by targeting the red-edge of the absorption band to uncover the effects of conformational heterogeneity on SF efficiency. Finally, we differentiated between two types of triplets generated through distinct pathways by analyzing TA kinetics across femtosecond to microsecond time scales. Overall, we anticipate that our investigation can offer molecular design principles for enhancing intramolecular singlet fission efficiency.

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(P-139)

Pulsed Laser Synthesis of NiCo Layered Double Hydroxides with Ru Doping for Enhanced OER Catalysis

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Two-dimensional layered double hydroxides (LDHs) have garnered significant attention as electrode materials due to their high activity, tunable composition, and unique structure. However, conventional synthesis processes require high temperatures and prolonged durations. In this study, we synthesized NiCo LDH using a pulsed laser rotation system, an eco-friendly and rapid synthesis method that can replace conventional high-temperature, high-pressure synthesis techniques. The morphology and composition of the synthesized LDH were confirmed through scanning electron microscopy (SEM) and SEM-EDS analysis, while the structural characteristics were investigated using X-ray diffraction (XRD) and Raman spectroscopy. Furthermore, Ru nanoparticles were doped into the NiCo LDH using a one-pot method with the same system. This material was then applied as a catalyst for the electrochemical oxygen evolution reaction (OER).

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(P-140)

Tracking electrospray process with X-ray Scattering

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Electrospray ionization (ESI) is a method to make a solution sample into gaseous ions by inducing Coulombic explosion of the sample droplets under strong electric field. While the droplets are getting smaller, unique molecular behaviors different from those in bulk solution appear, for example, fast diffusion and mixing in nanodroplets, and following accelerated reaction rates. However, since the nanodroplets are tiny, the detailed mechanism of these intriguing properties is not explored clearly so far. Here, we utilized ultra-short and super-bright X-ray pulse from X-ray free electron laser (XFEL), which enables us to observe samples of molecular-scales. We have developed a custom vacuum-ESI/X-ray scattering chamber to measure wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) to get structural information of Angstrom and sub-micrometer scale. Using this setup, we have been trying to obtain 1) size distribution of the nanodroplets and 2) unique molecular behaviors and their droplet-size dependence like regular assemblies by collecting WAXS and SAXS patterns simultaneously. We have successfully estimated the size of the nanodroplets and trying to find clues of molecular behaviors varying from the size of the nanodroplets.

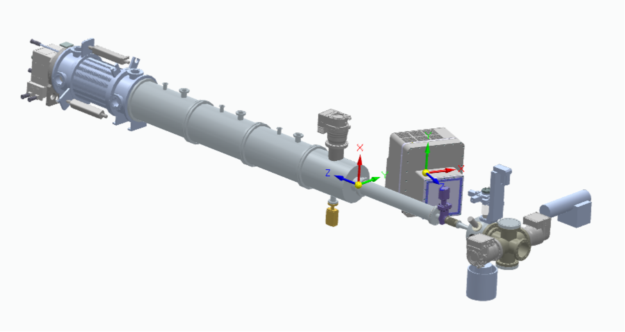

Figure 4 Vacuum-ESI/X-ray scattering setup

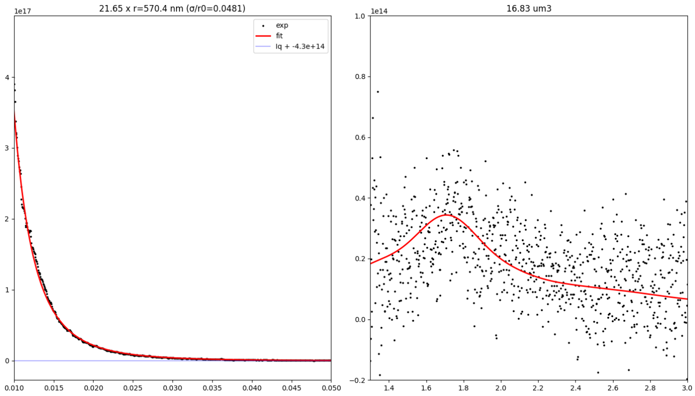

Figure 5 Estimated size of the nanodroplets (n=22, r=570 nm)

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(P-141)

Modeling Bacterial Stress Response Mechanisms: Implications for Cell Growth and Persistence

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Microorganisms adapt to harsh external environments by activating a variety of stress response signaling pathways crucial for their survival. Among these pathways, the general stress response is significant in bacteria, with the sigma factor RpoS being central to this network. Bacteria like Escherichia coli (***E. coli***) have developed mechanisms to rapidly respond to environmental stressors, including nutrient deprivation, oxidative stress, and osmotic stress. The activation of RpoS leads to a broad transcriptional response that enhances the bacteria's ability to withstand and recover from stress.

Studies examining bacterial population dynamics under stress often subject E. coli cultures to starvation and subsequent nutrient re-exposure. These experiments reveal that a subpopulation of bacteria, known as persisters, can survive prolonged stress. Persisters are phenotypic variants in a transient state of dormancy, making them highly tolerant to antibiotics and other stressors. Despite progress in understanding bacterial stress responses, a comprehensive understanding of the regulatory networks, particularly the role of RpoS in persister cell formation, remains incomplete.

In this study, we present a network model connecting the dynamics of RpoS to the formation and behavior of persister cells in E. coli. Our model integrates experimental observations to provide a quantitative framework for understanding RpoS-mediated stress responses and bacterial persistence. Developed from extensive experimental data, including RpoS levels, gene expression profiles, and persister cell counts under different stress conditions, the model simulates network dynamics to reproduce key observations. It suggests that fluctuations in RpoS levels are critical in determining the proportion of persister cells, linking stress response dynamics to long-term survival strategies.

This study advances our understanding of bacterial persistence, offering a quantitative explanation for RpoS's role in regulating phenotypic heterogeneity. These insights have important implications for developing strategies to combat chronic bacterial infections and design more effective antimicrobial therapies.

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Long-range corrected (LC) functional including a two-Gaussian Hartree-Fock operator (LC2gau-core-BOP) satisfying Koopmans' theorem for both inner and valence orbitals

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Previously, we reported a newly developed long-range corrected (LC) [1] density functional theory (DFT), named LC2gau-core-BOP [2], which can calculate the core excitation energies from 1s orbitals of both the 2nd- and 3rd-row atoms in high accuracy. The main point of LC2gau-BOP functional is that it includes an additional two flexible Gaussian function Hartree-Fock (HF) exchange to the LC functional. LC2gau-core-BOP shows deviations of less than 1.0 eV from experimental values for all the core-excitation energies of the tested molecules.

In this research, we will show that LC2gau-core-BOP satisfies Koopmans's theorem for core to valence orbitals of molecules including both the 2nd- and 3rd-row atoms by applying to ionization potentials of 63 small molecules of Chong, Gritsenko and Baerends (the CGB set) [3]. Moreover, we will present that LC2gau-core-BOP can perform well for core ionization energies of 2nd- and 3rd-row atoms. A notable feature of this study is that sophisticated inclusion of HF exchange integral depending on interelectronic distance may improve the performance of DFT functional on all the Koopmans' energies from core to valence orbitals.

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(P-143)

Effects of Energetic Disorder in Doped Conducting Polymer : Molecular Dynamics and Monte Carlo Study

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Applying dopants in organic semiconductors has been suggested as a convenient and powerful method to increase their electrical conductivity[1]. In such processes aimed at enhancing performance, understanding the underlying principles of doping plays a crucial role[2]. Among the various factors affecting electrical conductivity, the intrinsic energetic disorder of organic semiconductors has recently garnered significant attention[3,4]. However, limited theoretical or experimental characterization of their quantitative contributions to the overall conductivity has hindered molecular understanding of the underlying mechanism. In this study, theoretical approaches were employed to investigate how intrinsic energetic disorder affects conductivity. Initially, regioregular and regiorandom P3HT(Poly(3-hexylthiophene-2,5-diyl)) with $FeCl_3$ dopant molecules were modeled to simulate disordered organic semiconductor structures using molecular dynamics simulations. Subsequently, Metropolis Monte Carlo simulations were conducted to elucidate the relationship between Coulombic hole-anion interaction. Finally, kinetic Monte Carlo simulations for electron transfer were implemented to determine charge carrier mobility and transport energy of holes. Specifically, proposing the random movement of holes with charge transfer rates related to semiclassical Marcus theory[5,6] and transition state theory[6,7] facilitated the realistic modeling of the charge transfer process. Through these methods, we investigated the effects of intrinsic energetic disorder in organic semiconductors on each of the main processes

Seonghyeon Kang is currently a M.S. student in Prof. Chang Yun Son's group, Department of Chemistry, Pohang University of Science and Technology. His research interest is developing and applying charge transport simulation methods in various conductive materials.

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(P-144)

Computational analysis of G-quadruplex in structural transition process driven by cation types

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Single-stranded nucleic acids are highly flexible and can form a wide variety of conformations depending on conditions such as cations, pH, and crowding. Recent evidence suggests that the G-quadruplex (G4), a noncanonical DNA folding structure, is involved in numerous key genomic functions. The cations located in the core of G4 have attracted the most attention with respect to their structural stability. Nevertheless, due to limitations in resolution and resources, the detailed mechanisms of ion-dependent conformational changes in G4 have not yet been reported. In this study, we performed all-atom molecular dynamics (MD) simulations using two representative crystallographically determined G4 structures with identical sequences but different cations to elucidate the mechanisms of conformational transitions influenced by core cations. Using enhanced sampling method, we extensively explored the structural space between two representative crystals to collect numerous hybrid structures with their relative stability and observed structural preferences based on cation type. We aimed to identify the driving forces behind the conformational transition by decomposing its structural and energetic properties to characterize the key factors involved in multiple ion-centered folding and unfolding processes.

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(P-145)

Enhanced Microstructural Uniformity in Sulfuric Acid-Treated Poly(3,4-Ethylenedioxythiophene):Poly(Styrene Sulfonate) Films Using Raman Map Analysis

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Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) films have emerged as potential alternatives to indium tin oxide as transparent electrodes in optoelectronic devices because of their superior transparency, flexibility, and chemical doping stability.[1] However, pristine PEDOT:PSS films show low conductivities because the insulating PSS-rich domains isolate the conductive PEDOT-rich domains.[2] In this study, we present the conductivities and corresponding spatially resolved Raman properties of PEDOT:PSS thin films treated with various concentrations of H_2SO_4. After the PEDOT:PSS films are treated with the H_2SO_4 solutions, their electrical conductivities are significantly improved from 0.5 (non-treated) to 4358 S cm^{-1} (100% v/v). Raman heat maps of the peak shifts and widths of the $C_\alpha{=}C_\beta$ stretching mode are constructed. A blue shift and width decrease of the $C_\alpha{=}C_\beta$ Raman mode in PEDOT is uniformly observed in the entire measurement area (20 × 20 μm^2), indicating that microstructural transitions are successfully accomplished across the area from the coiled to linear conformation and high crystallinity upon H_2SO_4 treatment.[3] Thus, we prove that comprehensive Raman map analysis can be easily utilized to clarify microstructural properties distributed in large areas induced by various dopants. These results also offer valuable insights for evaluating and optimizing the performance of other conductive thin films.

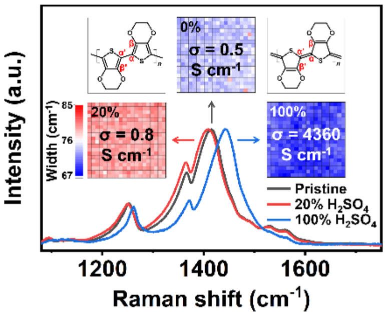

Figure 1. Raman mapping profile of PEDOT:PSS treated H_2SO_4 with different concentrations (0%, 20% and 100% v/v)

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(P-146)

Long-term Comparisons of Photoluminescence Affected by Organic Cations of Formamidinium and Methylammonium in Monophasic Lead Iodide Perovskite Quantum Dots

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This study compared the photoluminescence (PL) stabilities of formamidinium (FA) and methylammonium (MA) in lead iodide perovskite quantum dots (QDs). To exclude other factors, such as size and purity, that may affect stability, $MAPbI_3$ and $FAPbI_3$ QDs with nearly identical sizes (~10.0 nm) were synthesized by controlling the ligand concentration and synthesis temperature. Transmission electron microscopy images and X-ray diffraction patterns confirmed homogeneous single-phase perovskite structures. Additionally, the bandgaps and sizes of the synthesized QDs closely matched those of the infinite quantum well model, which guaranteed that the photostability was solely caused by the different organic molecules in the two QDs.[1,2] We analyzed the PL peak centers and full-width at half maximum of the QDs for 32 days. The enhanced stability of $FAPbI_3$ was found to be caused by the nearly zero redshift (1.615 eV) of its PL peak, in contrast to the redshift (1.685→1.670 eV) of that of $MAPbI_3$.

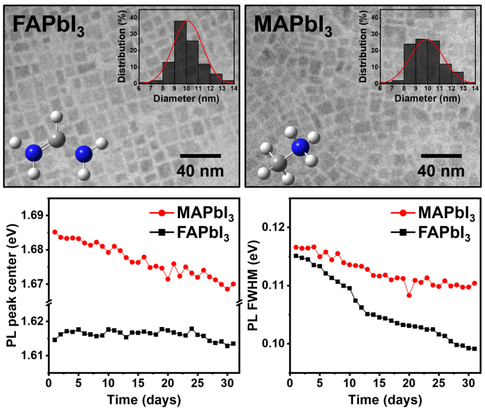

Figure 1. TEM images, size distribution (top), and PL stability monitoring (bottom) of $FAPbI_3$ and $MAPbI_3$ QDs.

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(P-147)

Optical Rashba Effect in α-$FAPbI_3$ Perovskite Enhanced by the Addition of MACl Additive

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The Rashba effect, which refers to the splitting of electronic spin polarized bands in momentum space of materials with broken inversion symmetry, is considered a promising phenomenon for the realization of spin-orbitronic devices. This is due to its potential possibility of manipulating electron spins in the semiconducting materials. In hybrid organic-inorganic perovskites, the Rashba splitting is particularly interesting yet controversial because of the symmetry ambiguity involving the presence or absence of an inversion center. Recently the optical Rasha effect has emerged as a promising tool for controlling the spin degeneracy of the system. By applying the circularly polarized optical pulse normal to the surface of semiconducting materials with strong spin-orbit coupling, the spin degeneracy can be lifted as a result of the broken inversion symmetry induced by the momentum selective optical pulse.

Despite its potential, only a few studies on the optical Rashba effect in Perovskite thin films have been reported. This is particularly because of the polycrystalline nature and random orientation of crystalline domains in perovskite thin films. However, recent advancements in additive engineering techniques have led to notable improvements in morphology and crystallinity of polycrystalline perovskite thin films.[1, 2] In particular, methylammonium chloride (MACl) has emerged as one of the most commonly used additives for achieving stable and efficient formamidinium lead tri-iodine ($FAPbI_3$) perovskite-based photovoltaics.

In this study, we prepared two different α-$FAPbI_3$ perovskite thin films, one with 10 mol% and the other with 40 mol% of MACl addition, to investigate the optical Rashba effect in polycrystalline perovskite thin films. Through circular polarization dependent femtosecond transient absorption microscopy measurement, we have observed distinct transient polarization decay profiles between two films. The $FAPbI_3$ films with 40 mol% MACl addition exhibited a high polarization value and a decaying constant of around 200 fs in 750 nm region, whereas the $FAPbI_3$ films with 10 mol% MACl addition showed a negligibly small initial polarization value. We assume that the higher directional crystallinity of the $FAPbI_3$ films with 40 mol% MACl addition, compared to that of 10 mol% film induce an efficient optical Rashba effect in $FAPbI_3$ films.

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(P-148)

Spatially-Varying Excitonic Behavior in CVD-grown MoS_2 Monolayer

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Introduction of Presenting Author

Nohyoon Park is an integrated PhD candidate in the combined UG-G program at the Department of Physics and Chemistry at DGIST. His primary interest lies in understanding the carrier dynamics in the two-dimensional transition metal dichalcogenides (2D TMDs) mainly using the femtosecond transient absorption microscopy (fs-TAM) technique. His poster presentation focuses on recent experiment results on spatially varying excitonic behavior in MoS_2 monolayer flake.

Abstract

Ceaseless efforts have been made to utilize 2D TMDs in the field of electronics, photonics, and catalysts as they are expected to exhibit excellent mechanical, optical, and electronic properties.[1, 2] However, despite its striking physical properties and versatility for a broad range of application, challenges still persist in fully harnessing their potential. One of the hurdles is the limited understanding of excitonic behavior within atomically thin TMD flakes. In this work, we aimed to understand the spatially varying behavior of exciton of CVD-grown MoS_2 by employing fs-TAM.

Interestingly, we observed a clear difference in optical properties between the edge and interior regions of the MoS_2 monolayer. While both A and B exciton bands appeared in both regions, their band intensities varied significantly across the probed areas. A strong A exciton peak was observed at the edge of the flake, with an intensity 2.5 times larger than that of the B exciton peak. However, this was not the case for the interior region, where the peak intensity of A exciton was massively suppressed while the peak intensity of B band remained the same. Spatially-varying A exciton behavior is clearly revealed in the transient absorption map obtained at 650 nm. A false-color map of the transient absorption peak at 650 nm reveals that the A exciton signal was dominant at the edge of the flake, further decaying within 10 ps.

This observation leads us to conclude that while A and B excitons behave independently and differ at the edge and interior regions, A excitons dominant at the edge of the flake. This allows us to conjecture that region-dependent exciton behavior will further inform strategies for enhancing the performance of optoelectronic devices. However, further investigation into the region-dependent quality or defects of MoS_2 flakes is necessary to understand the origin of the spatially varying exciton behavior.

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(P-149)

Structural dynamics of push-pull chromophores investigated by time-resolved impulsive stimulated Raman spectroscopy

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Time-resolved Raman spectroscopy has been proved as a useful analytical tool for the structural changes accompanying the excited state photochemical reactions occurring on ultrafast time scales [1,2]. We have recently reported the structural changes of several chromophores with π-conjugated backbones (stilbene, biphenyl, styrylpyran, etc.) by femtosecond stimulated Raman spectroscopy (FSRS) with both high spectral (<10 cm^{-1}) and temporal (<50 fs) resolutions, where the skeletal vibrational modes of ν_{8a} and $\nu_{C=C}$ were suggested as the sensitive probes of the structural changes related to the intramolecular charge transfer (ICT) [1,2].

In this work, we report the ICT dynamics of thioflavin T by impulsive stimulated Raman spectroscopy (ISRS). Thioflavin T is a well-known fluorescent dye used for the detection of amyloid fibrils associated with Alzheimer's diseases [3,4]. It has been widely acknowledged that the twist of the dimethylaminophenyl group (~90°) during ICT quenches the fluorescence of the locally-excited state, but direct experimental evidences for the identification of structural changes of thioflavin T is not available. In the ISRS results of thioflavin T in 1-ProH, we identified two kinetic components of ~370 fs and ~3.4 ps from the population dynamics and peak shifts originating from several in-plane and out-of-plane deformation modes of dimethylaminophenyl and benzothiazole backbones in the 400-650 cm^{-1} range. The population dynamics and peak shifts observed in these vibrational modes are interpreted as indicative of structural changes, such as the bend of the benzothiazole moiety and the twist of the dimethylaminophenyl group, based on the time-dependent density functional theory (TDDFT) calculations. Finally, we will also discuss preliminary ISRS results of the ICT dynamics of trisodium 8-aminopyrene-1,3,6-trisulfonate (APTS) and the associated structural changes probed in the low-frequency skeletal vibrational modes.

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(P-150)

Investigating lithium solvation structure in lithium-ion battery electrolytes with first principle force field

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The performance of rechargeable lithium-ion batteries, including their cyclability and thermal stability, is significantly influenced by electrolyte properties. Therefore, extensive efforts have been made to develop various electrolyte formulations to enhance battery performance. A comprehensive understanding of structural and dynamical properties is crucial for designing advanced electrolytes. Molecular dynamics (MD) simulations are a powerful tool for exploring ion coordination and clustering at the molecular level. Currently, various modeling approaches are used to simulate lithium-ion battery electrolytes, including non-polarizable and polarizable models.[1, 2] Non-polarizable models provide valuable insights into the dynamical and structural properties of electrolytes. However, for a precise understanding of ion-correlated motion, adopting an accurate polarizable model is essential.

In this study, we developed a transferable and predictive ab-initio polarizable force field for lithium-ion battery electrolytes, focusing on Li/EMIM/BF4 and LiPF6 in EC/DMC solvent systems. Our simulations accurately predicted lithium-ion clustering behavior in EC/DMC solvent. We found that clustering behavior in highly charged ionic liquid systems was significantly influenced by the force field, contrasting with simulations of neat ionic liquids. The dynamical properties also varied depending on the force field, with our polarizable model closely replicating experimental findings. Our results highlight the importance of using an accurate force field model for lithium-ion battery electrolytes and provide insights into cation-anion correlated motion, which could inform the design of 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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(P-151)

Two Fates of Peptide Isomerization Kinetics near Aqueous Interfaces

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Peptides at the interface have been explored in diverse range of applications ranging from nanomaterials to biomedical applications [1]. Especially, the molecular behavior of peptides at interfaces is deeply involved with the biocompatibility of a biomaterial such as biosensor, microelectronics, and antibody drugs [2]. It is therefore crucial to examine the stability of molecular conformations and the transition rates between conformation near interfaces, which are expected to be different from that of bulk due to the loss of solvation free energy. The lack of appropriate techniques to investigate the molecular behavior near aqueous interfaces calls for the computational methods to elucidate the interfacial effects on peptide conformational equilibria and isomerization kinetics.

In here, we leverage explicit-solvent classical MD simulation to elucidate the thermodynamic and kinetic behavior of solvated alanine dipeptide at aqueous interfaces (air-water, POPC-water, and octanol-water). Multidimensional free energy calculations show that the degree of stabilization near aqueous interfaces are different among conformations. Especially, the transition state TS1 that connects β(PPII, C5) state to αL state is relatively less stabilized at aqueous interfaces, whereas the transition state TS2 that connects β(PPII, C5) state to α state is relatively more stabilized at aqueous interfaces. Transition path sampling simulation combined with umbrella sampling (TPS+U)[3] shows that the isomerization rate constant for β(PPII, C5) state to αL state transition is suppressed by three times, whereas that for β(PPII, C5) state to α state transition is enhanced by three times. Energy decomposition analysis reveals that the two fates of the peptide isomerization kinetics are governed by the amount of the loss of solvation free energy near aqueous interfaces. TS1 conformation is more accessible to solvents due to its compact nature, which leads to the high solvation energy penalty near aqueous interfaces. For the TS2 conformation, however, the solvent-inaccessible nature of N-methyl hydrogen drops the solvation energy at bulk, which leads to strong stabilization at aqueous interfaces due to less solvation energy penalty.

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(P-152)

Enhancing Perovskite Solar Cell Performance: A Theoretical Exploration of Si-Substituted Spirobifluorene as Hole-Transporting Material

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Hybrid organic-inorganic perovskite solar cells (PSCs) are promising candidates for next-generation photovoltaics due to their high efficiencies. This study proposes a simple approach to enhance both the performance and stability of PSCs. We introduce Si-Spiro, a novel hole-transporting material (HTM) derived by substituting the central carbon atom in Spiro-OMeTAD with silicon. This modification leads to an increased hole mobility, a crucial factor for efficient charge transport. The superior performance of Si-Spiro compared to the reference Spiro-OMeTAD in PSCs is investigated through ab initio simulations. These calculations support the observed improvement by revealing Si-Spiro's favorable properties, including a low hole reorganization energy, low exciton binding energy, and high cohesive energy. Notably, Si-Spiro-based PSCs achieve a power conversion efficiency of 22.5%, exceeding the efficiency of devices using standard Spiro-OMeTAD. These findings suggest that Si-Spiro holds significant promise as a next-generation HTM for high-performing and stable PSCs.

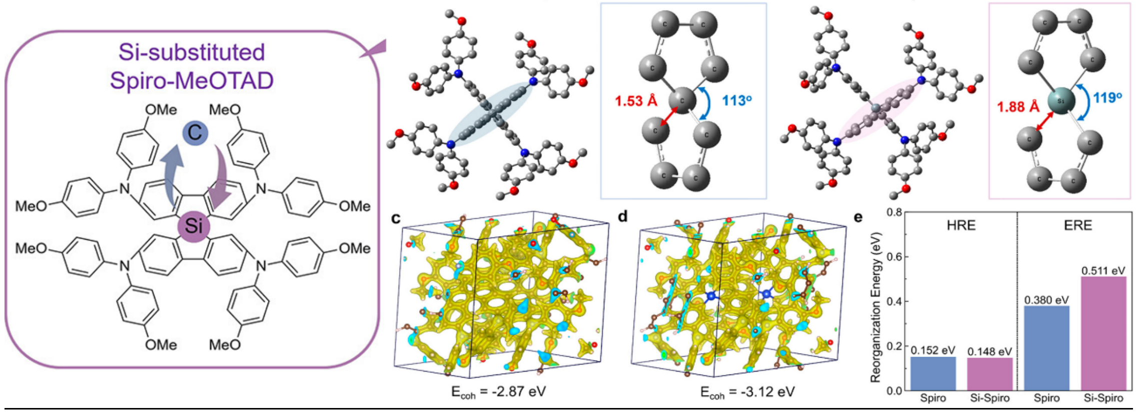

Figure. Molecular structure, charge density distribution, and hole-reorganization energies of Spiro-MeOTAD and Si-Spiro-MeOTAD.

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(P-153)

Characterizing preferential storage of medicinal biomaterials with transfer free energy calculations

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Designing functional biomaterials is of paramount importance, and lipid droplets (LDs), serving as essential intracellular organelles for lipid storage and transport, present a viable bio-mimetic platform for such innovation. These nano-scale interface domains not only insulate vital lipophilic substances like Zeaxanthin and Squalene, highlighting their biomedical application potential, but also act as characteristic interfaces in biology. Our goal is to utilize LDs as a platform for designing novel biomaterials. [1]

In this study, we aim to explore the stability of substrates that react with specific enzymes, utilizing lipid droplets (LDs) as a platform. The stability of substrates during their passage through the LD's phospholipid monolayer is influenced by their hydrophobicity or hydrophilicity, which is crucial for the enzymatic reactions within these organelles. Understanding this stability is essential, as it directly affects the productivity and efficiency of biotechnological applications.

To further our investigation, we seek to calculate the energy changes that occur when substrates translocate through the lipid droplet membrane using molecular dynamics (MD) simulation. By evaluating the free energy within individual domains, we aim to quantify the transfer free energy released during molecular migration. This will enable the calculation of partition coefficients for crucial substrates, essential for understanding compound interactions within the LD environment and enhancing our ability to predict and optimize productivity in bioengineering systems.

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(P-154)

Understanding the interphase properties based on conformation of polymer over various inorganic surfaces

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Epoxy resin which is a typical thermoset, is useful in many industry applications [1, 2]. For its many advantages such as good chemical resistance, excellent adhesion, dimensional stability, and so on. Diglycidyl ether bisphenol A (DGEBA) is one of the most widely used epoxy resins for coating the various materials. Although many types of epoxy-resin-based materials show good properties, but major failure modes include delamination at the epoxy resin-inorganic material interfaces, which has long been recognized as a critical limitation of such composites [3-6].

To understanding polymer/inorganic materials interfacial interaction, we check the conformations of adsorbed chains, which attached at the surface, are related to the macroscopic properties of the nanostructured systems [7]. Thus, figure out the properties of train, tail, and loop conformations of polymer chains in can explain a significant role of interphase in atomistic level. So, we will focus on the conformation of polymer over various lattice plane which can affects on the interaction [8].
In this study, the classical molecular dynamics (MD) simulation method was used to assess the conformation of DGEBA polymer over the chassis (α-Fe, α-Al2O3, and α-Fe2O3) higher than glass transition temperature with much longer than entanglement length. We study interfacial packing through the calculation of mass density profiles with specific functional groups. Then, investigate the conformation of adsorbed chains based on the radius of gyration and aspect ratio values in interphase region.

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(P-155)

Understanding Tertiary Structure of Donor-Acceptor Conjugated Polymers: Molecular Dynamics Simulation Insights

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Donor-acceptor conjugated polymers (DA CPs) received considerable attention for their electronic property. The structure of such polymers is expected to be an important factor in realizing their high electron mobility in electric devices. However, to our knowledge, no simulation study on the tertiary structure of conjugated polymer has been done. Backbone rigidity and side chain conformation are suggested to be important factors in determining such structures. In this work, we did molecular dynamics simulations of polymer melts and crystals with varying conformation of polymer backbone side chains. We used a force field developed by Ling Jiang et al[1] for DPP and T-TT conjugated core, and OPLS forcefield for other components of polymers. We found that the rigidity of the backbone chain makes the planar structure of DA CPs larger. We aim to find how backbone rigidity and side-chain engineering affect the crystallization and multi-level structure of DA CPs.

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(P-156)

Computational Study of Lithium Ion-Transport in TpBd-based Covalent Organic Frameworks

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2-Dimensional stacked Covalent Organic Frameworks(COFs) have emerged as important candidates for Lithium-ion conduction in energy devices[1]. Having an immobile anionic framework and mobile cations, they have a significantly higher transference number, compared to the conventional candidates. In this study, we investigate the ion-conduction in a sulfonated biphenyl COF structure, through the use of computational methods like Molecular Dynamics(MD) and Density Functional Theory(DFT).

We report the specific molecular mechanisms underpinning the ion-conduction pathways and the critical atomistic interactions responsible for the observed increase in the conductivity, compared to earlier reported systems from literature. We identified the presence of two distinct ion-channels and studied the movement of ions through these channels. We quantified the barriers for ion-motion in the corresponding channels by calculating the Free Energies involved in the process. Through the use of long-time MD simulations, we have calculated the conductivity of ions under the influence of an applied voltage and made a qualitative comparison of the values with earlier reported structures.

The difference in Lithium-Oxygen coordination structures in the ion channels, due to the addition of an extra phenyl group in the COF-backbone has been identified as an important factor in the increase in conductivity from earlier reported structures, offering critical insight and strategies to guide and improve the development of such systems and devices in the future.

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(P-157)

Advanced Detection and Characterization of Microplastics in Aqueous Environments Using Bright Field-Line Illumination Raman Microscopy

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Growing concerns regarding the environmental and human health impacts of microplastics necessitate improved detection and characterization methods. A significant amount of microplastic waste enters the environment and eventually makes its way into the oceans. While advancements in wastewater treatment technology mitigate some microplastic pollution, a significant portion persists in aquatic environments, as particles degrade below 1 micron and enter the nanoscale. Raman spectroscopy offers a valuable tool for microplastic analysis due to its low water interference, but its limited sensitivity presents challenges in observing the morphology of particles smaller than 5 microns. To address this, a comprehensive understanding of microplastics in aquatic environments and complementary techniques are necessary. We propose the application of bright field-line illumination Raman microscopy, enabling simultaneous analysis of both chemical composition and morphology. Our study successfully employed this method to observe and distinguish between three types of microplastics (polypropylene, polyethylene, and poly(methyl methacrylate)) ranging from 0.7 to 10 microns in water. Further, machine learning integration facilitated accurate material differentiation. This approach demonstrates significant potential for practical application in environmental monitoring and microplastic detection within aquatic ecosystems.

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(P-158)

Microplastics Analysis with Macro-scale Hyper Raman Imaging system

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The extensive use of plastic materials, driven by their numerous advantageous properties, has resulted in a substantial surge in plastic consumption, and as a result, there has been a significant increase in the generation of primary and secondary microplastics. Microplastics are typically plastic particles or fragments that are less than 5 mm size. As concerns regarding the adverse impacts of microplastics on ecosystems and human health continue to escalate, there is a growing interest in microplastic analysis. In response to this, our study has developed a macro-scale hyperspectral Raman method aimed at swiftly quantifying and characterizing substantial volumes of plastics.

By implementing this approach, we achieved remarkable success, obtaining Raman spectra for five different types of microplastics scattered over a 1.5 cm2 area in a mere 1000 seconds. Utilizing a machine learning method, we demonstrated the effectiveness in acquiring Raman spectra, even when microplastics are suspended in aquatic environment or adhered to metal mesh nets. These findings underscore the significant potential of our developed method for practical real-world applications.

We are currently conducting experiments aimed at classifying microplastics, even when they are trapped on cellulose filters, utilizing this system. Our objective is to achieve classification of microplastics present in authentic natural samples.

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(P-159)

Narrowing Nanogaps of Gold Nanoparticle Assemblies Using Plasma Treatment

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Nanogaps between the nanoparticles that constitute a nanoassembly determine the plasmonic properties of the nanoassembly. For instance, the nanogap distance tunes the resonance frequency of the optical response of the nanoassembly through plasmon coupling.[1] Surface-enhanced Raman scattering is enabled only by the presence of nanogaps.[2] Generation of hot carriers is significantly promoted in nanogap areas. Therefore, control of nanogaps is the key to the advancement of plasmonics. In this study, we find that plasma treatment is an effective way to narrow the nanogaps and eventually sinter the nanoparticles, leading to the production of newly shaped nanoassemblies. We synthesize 55 nm spherical gold nanoparticles (AuNSs) and assemble them into homodimers using a molecular linker with a distance of 1.3 nm. As we apply plasma, we observe that the plasmon coupling peak gradually redshifts, weakens, and then turns around to a blueshift and strengthens. Comparison of electron microscopy images reveals that plasma treatment narrows the nanogaps and causes the nanoparticles to merge. We prepare various nanoassemblies including heterodimers and core@satellite nanostructures using AuNSs, gold nanorods (AuNRs), and gold nanocubes (AuNCs). Applying plasma treatment to these nanoassemblies produces a new class of merged nanoparticles that have different plasmonic properties than nanoassemblies with gaps.

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(P-160)

Spotting Hot Carrier Ejection Sites on Gold Nanocubes

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The field of plasmonics began to grow explosively in the early 2000s and is still growing steadily on account of fascinating beneficial properties for applications like photovoltaics, photocatalysis, and high-performance sensor. Even though the explosive growth of plasmonics was made, still many unsolved questions remain. Where is the hot charge carrier generated by interaction of light with plasmon ejected is one of those veiled questions. In this study, we explored which site is the most active in generating and ejecting hot carriers through plasmonic reduction reaction. The reaction of choice was the reduction of silver ions to solid on gold nanocube which have flat faces and highly curve edges as well as vertices: $Ag^+(aq)$ + plasmonic hot e− → $Ag(s)$. We observe that silver precipitates formed more actively on the surfaces around corners and edges of gold nanocube.

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Transport Dynamics of Water Molecules nanoconfined between phospholipid bilayers.

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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 present a novel transport equation for water molecules in the intermembrane space [1], providing a quantitative explanation for molecular dynamics (MD) simulation results. Our findings reveal that the unique transport dynamics of water molecules comes from the fluctuations in the lateral diffusion coefficient, influenced by their longitudinal motion perpendicular to the membranes. Additionally, we identify an interfacial region where water exhibits unique physical properties, remaining unaffected by variations in the intermembrane distance.

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(P-162)

Universal Thermal Properties and Scaling Behaviors in the Coil-to-Globule Transition of a Single Chain

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Using parallel tempering molecular dynamics (PTMD) simulation with a bead spring polymer model, we investigate universal features in the thermal properties of single chains observed during the coil-to-globule transition. We find that as the temperature $\boldsymbol{T}$ decreases, the conformational transition of a single-chain polymer takes place from a coiled state to a globule state. Upon temperature variation, the heat capacity $\boldsymbol{C_v}$ exhibit a shoulder structure rather than a sharp peak, reflecting the continuous nature of the phase transition. We determine the shoulder point of $\boldsymbol{C_v}$ as the coil-to-globule transition temperature $\boldsymbol{T_{cg}}$. Our results demonstrate that as the chain length $\boldsymbol{N}$ increases to infinity, $\boldsymbol{T_{cg}}$ converge to the theta temperature $\boldsymbol{\Theta}$, where the attractive and repulsive interactions of monomers are balanced. At $\boldsymbol{T = \Theta}$, $\boldsymbol{C_v}$ exhibits a scaling behavior with $\boldsymbol{N}$, i.e., $\boldsymbol{C_v \sim N(\ln N)^{3/11}}$, as predicted by previous renormalization group theories considering many-body interaction of the monomers. More interestingly, when $\boldsymbol{C_v}$ of various $\boldsymbol{N}$ is rescaled by a factor of $\boldsymbol{N(\ln N)^{3/11}}$, $\boldsymbol{C_v}$ collapses onto a single curve with respect to a broad range of $\boldsymbol{T}$, while changing $\boldsymbol{N}$ from 100 to 3000. This indicates that the many-body interactions should be importantly considered for examining the universal feature of the coil-to-globule transition.

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Universality Feature of Transport Distribution in Percolation

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Transport phenomena arising from emerging percolating clusters display universal critical behaviors. Universal scaling relations are well-established for average transport properties by conventional percolation theory, but in this work, we explore the universality in their distributions. Specifically, we probe the electrical conductivity in percolating clusters and discover a new aspect of universality in its distribution. When approaching the percolation threshold, there is a distinct crossover from a non-Gaussian to a Gaussian distribution shape. Surprisingly, the non-Gaussian transport distribution near the threshold shows universal finite-size scaling. Our research suggests a potential connection between extreme value statistics and the universal behavior of transport distributions. Both the average and the distribution of electrical conductivity belong to the same universality class, governed by the same transport exponent, revealing a shared universal principle. These findings provide valuable insights into universal features found in the distribution of different transport phenomena that appeared by percolating clusters, opening new methods to analyze transport in a wide range of percolation-based systems.

(P-164)

Temperature Dependence of Thermal Conductivity in Supercooled Liquids

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We investigate the temperature dependence of the thermal conductivity of supercooled liquids using Molecular Dynamics (MD) simulations. We employ the Kob-Andersen (KA) binary liquids as a model system and calculate the thermal conductivity $\boldsymbol{\lambda}$ at various temperatures $\boldsymbol{T}$ using the Green-Kubo (GK) formalism. Our results show that as $\boldsymbol{T}$ decreases below the onset temperature $\boldsymbol{T_{onset}}$, the structural relaxations of KA liquids become sluggish, leading to subdiffusive regimes in the mean-squared displacement and a clear separation between $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ relaxations in the intermediate scattering functions. Despite these changes, $\boldsymbol{\lambda}$ consistently follows a scaling relation with $\boldsymbol{T}$, specifically $\boldsymbol{\lambda \sim T^{1/4}}$ across all temperature ranges. We find that the auto-correlation function of the heat flux in the GK formalism vanishes over a very short time scale compared to the structural relaxation time, indicating that heat conduction occurs over short time scales associated with local dynamics and structures. This may explain why the temperature dependence of thermal conductivity is minimally affected by the long-time scale structural relaxation of glassy liquids.

(P-165)

Inter-chain Hydrogen Bonding Effects on Chemical Stability of Self-Assembled Monolayers

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This study explores the impact of heat on self-assembled monolayers (SAM), with a focus on investigating thermal stability as a crucial factor influencing their functionality. To improve thermal stability, we introduced hydrogen-bonds through amide groups, significantly enhancing the intermolecular interactions among SAM monomers compared to alkanethiol-based SAMs. Utilizing vibrational sum-frequency-generation (VSFG) spectroscopy, a non-invasive technique well-suited for analyzing surface structures at elevated temperatures, our in-situ experiments on N-(2-mercaptoethyl)heptanamide-SAM revealed its distinctive thermal behavior. Notably, the incorporation of amide groups did not enhance the heat resistance of the SAMs; instead, liquid-like properties were observed. Furthermore, these amide-derivatized SAMs exhibited parallel and anti-parallel β-sheet-like H-bonding structures, dynamically transitioning during heating and cooling. These findings underscore the intricate relationship between molecular structure and thermal stability, providing valuable insights for the future application of SAM in scientific and industrial domains.

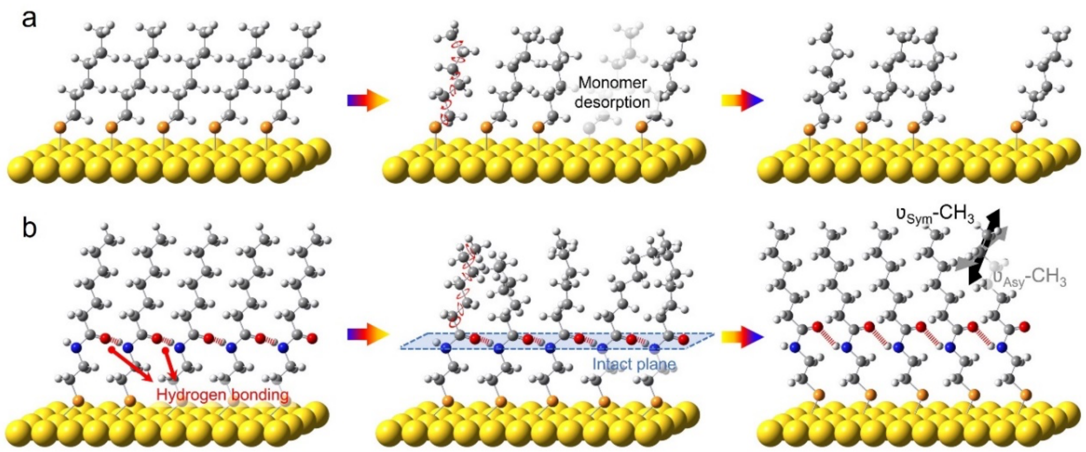

Figure 2. Schematic illustration of heat-induced structure transformation in SAMs

(P-166)

Circular Dichroism Spectroscopy of Ubiquitin Ion in the Gas Phase

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Circular dichroism (CD) spectroscopy is widely used for the structural analysis of proteins. Numerous studies have been carried out to date, with most conducted in the condensed phase. However, research in the condensed phase has several limitations: First, it is difficult to determine which charge state of a protein with multiple charge states exhibits CD. Second, proteins are thought to exist in multiple conformers due to their large size, but only an averaged CD spectrum can be obtained. CD spectroscopy of proteins in the gas phase can overcome these drawbacks. Charge state and conformer-specific CD spectra can aid in understanding the structure of relatively small molecules (less than 40 kDa) that are difficult to observe through microscopy. Despite these advantages, the CD spectrum of proteins in the gas phase remains unknown. Most studies have focused on small molecules[1,2], with only a few addressing relatively large molecules[3]. Herein, we present the first CD spectrum of proteins in the gas phase. CD spectra of multiple charge states of ubiquitin in the region of the origin band were mainly presented. Our novel technique for obtaining CD spectra, named the dual-beam method[4], was used. In this method, a linearly polarized reference beam was used to correct the circularly polarized main beam. This study demonstrates that CD spectroscopy of proteins in the gas phase can provide structural information specific to charge state and conformers.

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