



# **Nanomaterials Chemistry Workshop 2024**

**April 4-5, 2024**

**@Joint Research Laboratory Building  
Uji Campus, Kyoto University**

**Sponsored by  
International Joint Usage/Research Center (iJURC),  
Institute for Chemical Research, Kyoto University**



## Scientific Program

### April 4 (Thursday)

13:20-13:30 Welcome Remarks & Introduction of iJURC  
Toshiharu TERANISHI (Kyoto Univ.)

**Chair: Tatsuya TSUKUDA**

13:30-14:00 “Surface Engineering of Metallic Nanocrystals via Atomic Structure and Composition Control for Boosting Electrocatalysis”  
Sang Woo HAN (KAIST)

14:00-14:30 “Platinum Group Metal-Based Solid-Solution Alloy Nanocrystals: Binary to High-Entropy Alloys”  
Hiroshi KITAGAWA (Kyoto Univ.)

14:30-15:00 “Designed Synthesis and Assembly of Inorganic Nanomaterials for Energy and Catalytic Applications”  
Taeghwan HYEON (Seoul National Univ.)

15:00-15:30 “Transformation and Advanced Properties of Isolated and Assembled Ionic Nanocrystals”  
Toshiharu TERANISHI (Kyoto Univ.)

15:30-15:45 Break

**Chair: Jinwoo CHEON**

15:45-16:15 “Nanoclusters and Quantum Dots”  
Sungjee KIM (POSTECH)

16:15-16:45 “Stability-Function Relationship in Molecular Electronics”  
Hyo Jae YOON (Korea Univ.)

16:45-17:15 “Metal-Organic Frameworks for Advanced Polymers”  
Takashi UEMURA (Univ. Tokyo)

17:15-17:30 Discussion Today’s all speakers

## April 5 (Friday)

**Chair: Toshiharu TERANISHI**

09:30-10:00 "Porous Ionic Crystals Based on Metal-Oxo Clusters as a Platform for Functional Materials"  
Sayaka UCHIDA (Univ. Tokyo)

10:00-10:30 "Chemical Nanoplasmonics: From Nanoparticle Synthesis to Surface-Enhanced Spectroscopic and Bidiagnostic Applications"  
Jwa-Min NAM (Seoul National Univ.)

10:30-11:00 "STM Studies of Plasmon-induced Chemical Reactions at a Single-molecule Level"  
Emiko KAZUMA (Univ. Tokyo)

11:00-11:15 Break

**Chair: Jwa-Min NAM**

11:15-11:45 "Designer Nanomachines for Biological Systems"  
Jinwoo CHEON (Yonsei Univ.)

11:45-12:15 "Single-Atom Signaling and Metalloallostery: Bioinorganic Chemistry Beyond Active Sites"  
Christopher J. CHANG (Univ. California, Berkeley)

12:15-12:45 "Atomically Precise Gold Clusters as Model Catalysts"  
Tatsuya TSUKUDA (Univ. Tokyo)

12:45-13:00 Discussion Today's all speakers

13:00-13:05 Concluding Remarks  
Tatsuya TSUKUDA (Univ. Tokyo)

## Access & Venue



- **From the Airport to Kyoto Station**

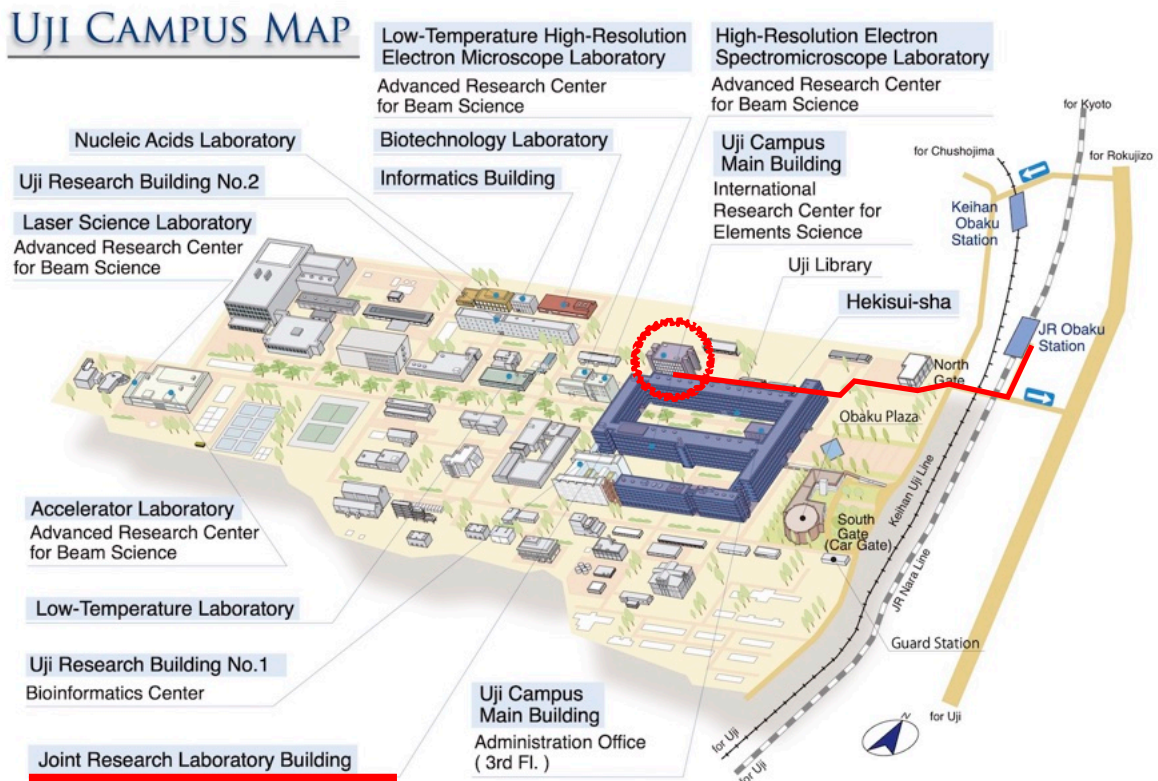
see [https://www.kuicr.kyoto-u.ac.jp/sites/icr/about/access/to\\_kyoto\\_station/](https://www.kuicr.kyoto-u.ac.jp/sites/icr/about/access/to_kyoto_station/)

- **From Kyoto Station to Venue (Uji Campus)**

JR Kyoto to Obaku station: ~20 min

(every 15 min; platforms 8-10; take a local train, NOT a rapid train)

JR Obaku station to venue: ~5 min walk



## Abstract

### **Surface Engineering of Metallic Nanocrystals via Atomic Structure and Composition Control for Boosting Electrocatalysis**

Sang Woo HAN (Korea Advanced Institute of Science and Technology)



Since the clean energy industry emerged, developing efficient nanocrystal catalysts has attracted ever-increasing attention. Recently, the utilization of metal nanocrystals as catalysts for electrochemical reactions is entering a new era with the development of theories and techniques that help incorporate surface chemistry into nanoscale materials. Current approaches in the field of nanocrystal catalysts include detailed analyses and modifications of the surface atoms of nanocrystals, with which optimal structures and compositions for target electrochemical reactions could be realized. In this presentation, I introduce recently developed strategies to engineer the surface structure of nanocrystals through control over the atomic arrangement and composition of nanocrystal surfaces for boosting electrocatalysis.

### **Platinum Group Metal-Based Solid-Solution Alloy Nanocrystals: Binary to High-Entropy Alloys**

Hiroshi KITAGAWA (Kyoto University)



Platinum group metal (PGM) nanoparticles (NPs) have been investigated in a variety of research fields such as catalysis and electronics. Among the types of alloys, solid-solution alloy NPs have the advantage of being capable of continuously changing their properties by tuning their composition. However, synthesizing PGM solid-solution alloy NPs with any combination and composition is not an easy task due to the metallurgical aspects. In this work, we have focused on PGM-based solid-solution alloy NPs, and in particular those with immiscible alloy systems.

The physical and chemical properties of most solids are strongly correlated to their electronic structure, in particular the DOS at the  $E_F$ . In 2015, we proposed the “DOS engineering” concept for designing materials, which calls for the control not only of the location of the d-band center, but also of a suitable DOS shape, such as the band width and the DOS shape of unoccupied and occupied states around  $E_F$ . We propose that by means of “interelement fusion,” where the elemental periodic table is colored by the  $s$ ,  $p$ ,  $d$ , and  $f$  groups, it is possible to manipulate the shape of the DOS freely by choosing elements from the  $s$ ,  $p$ ,  $d$ , and  $f$  groups according to the properties desired.

## Designed Synthesis and Assembly of Inorganic Nanomaterials for Energy and Catalytic Applications

Taeghwan HYEON (Seoul National University)



Recently we have focused on the architecture engineering of inorganic nanomaterials for their applications to electrocatalysis and photocatalysis. We present a synthesis of highly durable and active fuel cell electrocatalysts based on ordered M-Pt alloy nanoparticles for oxygen reduction reaction (ORR) in PEMFC. We synthesized highly active and stable electrocatalysts for hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) production including Co- $\text{N}_4(\text{O})$  moiety incorporated in nitrogen-doped graphene ( $\text{Co}_1\text{-NG}(\text{O})$ ) and cobalt phthalocyanine (CoPc) immobilized on oxidized carbon nanotube substrate. The electrocatalytic oxygen evolution reaction (OER) plays a pivotal role in the mass production of hydrogen fuel and chemical feedstocks by various electrochemical reactions. We report that early transition metals with vacant d orbitals ( $d^0$ -oxoanions) directly participate in and accelerate the alkaline OER via a redox cycle associated with early transition metal-peroxo species. We demonstrate that active machine-learning on even small datasets can discover a “champion” four-metal perovskite oxide OER catalyst. We report on the design and synthesis of highly active  $\text{TiO}_2$  photocatalysts incorporated with site-specific single copper atoms that exhibit high photocatalytic hydrogen generation and  $\text{CO}_2$  photoreduction activity. We presented a floatable photocatalytic platform constructed from elastomer-hydrogel nanocomposites, demonstrating its superiority over conventional systems in solar hydrogen production. We demonstrated a general method for synthesizing atomically dispersed catalysts via photochemical defect tuning for controlling oxygen vacancy dynamics.

## Transformation and Advanced Properties of Isolated and Assembled Ionic Nanocrystals

Toshiharu TERANISHI (Kyoto University)



Elaborate chemical synthesis methods allow the production of various types of inorganic nanocrystals (NCs) with uniform shape and size distributions. Then, how can we synthesize NCs with thermodynamically metastable phases or very complex structures? The transformation of already-synthesized NCs via elemental substitutions, such as ion exchange reactions for ionic NCs and galvanic replacement reactions for metal NCs, can overcome the difficulties facing conventional one-step syntheses. In particular, NC ion exchange reactions have been studied with numerous combinations of foreign ions and ionic NCs with various shapes. The functionality of the resulting ionic NCs, including semiconducting and plasmonic properties, can be easily tuned in a wide range, from the visible to near-infrared. Here we focus on the full ion exchange reactions involving ionic NCs and NC superlattices, highlighting important aspects such as the preservation of appearance and dimensions. Finally, we show the advanced optical properties of cation-exchanged NCs and concerted optical properties of NC superlattices.

## Nanoclusters and Quantum Dots

Sungjee Kim (POSTECH)



Magic sized clusters (MSCs) are thermodynamically stable intermediate nanoclusters often captured during the growth of semiconductor nanoparticles (NPs). MSCs can be isolated as intermediates in quantum dot (QD) synthesis, and they provide pivotal clues in understanding QD growth mechanisms. We report syntheses for two families of heterogeneous-atom-incorporated InP MSCs that have halide or zinc atoms. All the MSCs could be directly synthesized from conventional molecular precursors. Alternatively, each series of MSCs could be prepared by sequential conversions. As the conversion proceeded, evolution from uni-molecule-like to QD-like characters was observed. Early stage MSCs showed active inter-state conversions in the excited states, which is characteristics of small molecules. Later stage MSCs exhibited narrow photoinduced absorptions at lower-energy region like QDs. The crystal structure also gradually evolved from polytwistane to more zinc-blende. We also introduced halide atoms (Cl, Br, I) as dopants into MSCs. Chiroptical activities of III-V group QD growth intermediates, or MSCs, will be addressed as suggesting chiral MSCs as prospective materials on designing chiroptical nanomaterials. InP nanoparticles and nanostructures synthesized from InP MSCs will be also discussed.

## Stability-Function Relationship in Molecular Electronics

Hyo Jae YOON (Korea University)



In the field of molecular electronics, the stability of the active component, specifically, self-assembled monolayer (SAM), exerts a significant influence over the functionality of the corresponding molecular tunnel junction. The number and types of molecular orbitals that enter external bias windows dictate the shape of the current-voltage curve and the magnitude of current flowing through the junction. Moreover, in thermoelectric molecular junctions, the asymmetry in the hole-electron density of states (DOS) is influenced by the amount of heat applied to the junction. Consequently, the inherent instability of conventional SAMs poses a formidable obstacle to fully understanding the mechanisms underlying charge transport through organic matters and hinders the development of novel functionalities. Addressing this challenge, our research group has recently devised strategies grounded in supramolecular and organometallic approaches to bolster the electrical and thermal stability of SAMs on noble-metal surfaces. The remarkable improvements in stability have enabled us to explore charge tunneling across unprecedentedly wide bias windows and delve into the atomic-level intricacies of the Seebeck effect at substantially elevated temperature ranges. These significant findings will be described in detail in this presentation.

## **Metal-Organic Frameworks for Advanced Polymers**

Takashi UEMURA (The University of Tokyo)



Metal-Organic Frameworks (MOFs) composed of metal ions and organic ligands have been extensively studied. The characteristic features of MOFs are highly regular channel structures with controllable pore sizes approximating molecular dimensions and designable surface functionality. Thus, MOFs have been successfully applied in numerous domains, including storage and separation, catalysis, energy, and sensing. However, the majority of relative studies in the early stages of MOF research focused on gas and solvent molecules as guests, despite the potential of infinite nanochannel structures for the encapsulation of macromolecules.

Since 2005, we have utilized the regular and tunable channels of MOFs for a field of polymerization, which can allow multi-level controls of polymers, nanoparticles, and nanographenes. In addition, construction of nanocomposites between MOFs and polymers provides unprecedented material platforms to accomplish many nanoscale function. We have also developed direct insertion of polymers into nanochannels of MOFs, which enables powerful macromolecular recognition and separation technologies with exceptionally high selectivity. Designing nano-sized pores of MOFs with a regular arrangement of reactive/interactive/responsive entities offers the possibility of universal polymer production and purification that cannot be accomplished by conventional methods.



## **Porous Ionic Crystals Based on Metal-Oxo Clusters as a Platform for Functional Materials**

Sayaka UCHIDA (The University of Tokyo)



Porous crystalline materials such as zeolites and metal-organic frameworks (MOFs) have attracted wide attention due to their well-defined porous structures and high surface area, which are useful in gas storage and separation, ion exchange and conduction, and heterogeneous catalysis. Polyoxometalates (POMs) are nano-sized anionic metal-oxo clusters with unique catalytic, electrochemical, magnetic, and luminescent properties. We have reported that the complexation of POMs with molecular cations with appropriate elements, charges, sizes, symmetry, ligands, etc., results in the formation of voids and channels in the crystal lattice. The properties of porous ionic crystals (PICs) based on POMs can be summarized as follows. (a) POMs show reversible redox properties, which can lead to the formation of “redox-active” PICs. (b) Guest binding and catalytically active sites can be incorporated beforehand into the ionic components. These functions can be maintained and utilized in the PICs since the ionic components remain as discrete molecules in the crystal lattice. (c) POMs can transport protons as counter cations efficiently because the negative charge of POMs is smeared over the external oxygen atoms, reducing the effective surface charge density. These properties lead to interesting functions in selective ion-uptake/exchange, proton conduction, heterogeneous catalysis, formation of luminescent mixed-valence metal clusters, etc., which are unique to PICs.

## **Chemical Nanoplasmonics: From Nanoparticle Synthesis to Surface-Enhanced Spectroscopic and Biodiagnostic Applications**

Jwa-Min NAM (Seoul National University)



Plasmonics deals with understanding and manipulating the interaction between light and matter at a scale that is significantly smaller than the wavelength of light (e.g., metal nanoparticles), and chemical nanoplasmonics is mainly about the study and use of nanoscale chemistry for advancing plasmonics and the use of plasmonics to address key issues and challenges in chemistry and other related fields. Designing, synthesizing and controlling metal nanostructures with a superhigh precision for a large number of structures are the keys to the reliable and widespread use of plasmonic nanostructures in chemistry, materials science, optics, nanoscience, biotechnology and medicine. Here, I will share the design, synthetic strategies and characterization results of molecularly tunable and structurally reproducible plasmonic nanostructures including metal nanogap structures, multi-component metal nanoparticles and gold nanocatenanes with strong, controllable and quantifiable plasmonic signals (e.g., quantitative surface-enhanced Raman scattering). I will then show their potential in addressing some of important challenges in plasmonics, biosensing, bioimaging and therapeutics, and discuss how these new plasmonic materials and platforms can lead us to new breakthroughs in nanochemistry, next-generation disease diagnostics, molecular computing and nanomachines/nanorobotics.

## STM Studies of Plasmon-induced Chemical Reactions at a Single-molecule Level

Emiko KAZUMA (The University of Tokyo)



Localized surface plasmons of metal nanostructures enable the efficient use of solar light and have been used for various applications such as local spectroscopies, sensing, photovoltaics, fluorescence enhancement, and photocatalysts. Among the various applications, plasmon-induced chemical reactions are attracting increasing researchers' attention as novel photocatalytic reactions. During the excitation and decay processes of the plasmons, strong electric fields, hot carriers, and heat are generated and can serve as excitation sources for the molecules, and thus several reaction mechanisms have been proposed. However, the reaction mechanism remains to be fully elucidated due to the difficulty of direct observation of the chemical reactions in the plasmonic field strongly localized near the metal surface. A scanning tunneling microscope (STM) combined with optical excitation by light can be used to investigate plasmon-induced chemical reactions on metal surfaces. This technique provides insights into the mechanism and pathways of the plasmon-induced chemical reactions at a single-molecule level, which cannot be obtained by conventional macroscopic methods. Our single-molecule studies reveal that the degree of the orbital hybridization at the metal–molecule interface affects the molecular excitation by the plasmons and determines the dominant excitation mechanism.

## Designer Nanomachines for Biological Systems

Jinwoo CHEON (Yonsei University)



One of the important trends of next-generation biomedical sciences is the development of new tools that can accurately image, identify, and execute desired missions in a selectively programmed manner for biological systems. In this talk, I will discuss the design of nanomachines as platform tools for a variety of functionalities such as sensing targeting and signaling of cells and live animals in a selective and efficient way. These tools serve not only as a contrast agent for highly accurate MR imaging but also as a modulator for cell signaling of neurons via magneto-genetics for the behavior control of live animals. This is a new approach of controlling neurons via magnetism which will serve for deep brain stimulations via remote and wireless neuromodulations.

[References]

1. Lin, M., Lungerich, D., Cheon, J. et al. "A magnetically powered nanomachine with a DNA clutch" *Nat. Nanotechnol.*, **2024**. online published.
2. Kim, W.-S., Shapiro, M. G., Cheon, J. et al. "Magneto-acoustic protein nanostructures for non-invasive imaging of tissue mechanics in vivo" *Nat. Mater.*, **2024**, 23, 290.
3. Lee, J.; Cheon, J. et al. "Non-contact long-range magnetic stimulation of mechanosensitive ion channels in freely moving animals" *Nat. Mater.*, **2021**, 20, 1029.
4. Shin, T.; Choi, B.; Cheon, J. et al. "High-resolution T1 MRI via renally clearable dextran nanoparticles with an iron oxide shell" *Nat. Biomed. Eng.*, **2021**, 5, 252.

## Single-Atom Signaling and Metalloallostery: Bioinorganic Chemistry Beyond Active Sites

Christopher J. CHANG (University of California, Berkeley)



Metals in biology play essential roles in health and disease as they span a unique continuum from metabolism to signaling. Motivated to study metals in their native biological contexts and how they are misregulated in disease, we are developing molecular imaging probes to track dynamic metal pools with spatial and temporal resolution and proteomics probes to characterize metal-dependent targets of cell signaling. This presentation will focus on our latest work in the development of metal-responsive sensors and their application to decipher single-atom transition metal signaling pathways and metalloallostery in fundamental behaviors such as eating and sleeping.

## Atomically Precise Gold Clusters as Model Catalysts

Tatsuya TSUKUDA (The University of Tokyo)



Gold clusters protected by organic ligands, stabilized by polymer, and immobilized by solid supports have provided ideal platforms to study the correlation between various structure parameters and catalytic properties. This talk will introduce precision synthesis and structural characterization of Au clusters and discuss how the catalytic performances are affected by key structural parameters such as size, doping, and surface modification. These fundamental studies will establish a guiding principle to design and optimize the catalytic properties of Au-based clusters. The topic includes the following recent examples:

- (1) Photocatalysis by phosphine-protected  $\text{MAu}_{12}$  ( $M = \text{Au}, \text{Pd}, \text{Rh}, \text{Ir}, \text{Pt}$ ) [1, 2].
- (2) Electrocatalysis by N-heterocyclic carbene-protected  $\text{Au}_{11}$  [3] and  $\text{Au}_{24}$  [4].
- (3) Alcohol oxidation by poly(*N*-vinyl-2-pyrrolidone)-stabilized  $\text{Au}_{24}$  [5],  $\text{Au}_{38}$  [6] and  $\text{Au}_{23}\text{Pd}_1$  [7].
- (4) Alcohol oxidation by  $\text{Au}_{25}$  supported on double metal hydroxide [8], partially thiolated  $\text{Au}_{25}$  anchored on carbon [9], and partially thiolated  $\text{Au}_n$  ( $n = 25, 102$ ) on layered double hydroxide [10].

[References]

- [1] *ChemElectroChem*. **11**, e202300669 (2024). [2] *Angew. Chem., Int. Ed.* **61**, e202207290 (2022). [3] *Nature Chem.* **11**, 419–425 (2019). [4] *J. Am. Chem. Soc.* **144**, 9000–9006 (2022). [5] *JACS Au* **1**, 660–668 (2021). [6] *ACS Catal.* **12**, 6550–6558 (2022). [7] *ACS Nano* **16**, 16932–16940 (2022). [8] *Nanoscale* **14**, 3031–3039 (2022). [9] *ACS Catal.* **13**, 3263–3271 (2023). [10] *ACS Catal.* **13**, 16179–16187 (2023).