Symposium | Asian International Symposium : Asian International Symposium - Photochemistry -

iii Sat. Mar 29, 2025 9:00 AM - 11:40 AM JST | Sat. Mar 29, 2025 12:00 AM - 2:40 AM UTC **ii** [A]D302(D302, Bldg. 4, Area 3 [3F])

[[A]D302-4am] Asian International Symposium - Photochemistry -

Chair, Symposium organizer: Mitsuaki Yamauchi, Yoichi Kobayashi, Sadahiro Masuo

9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC

Opening Remarks

● English ● Invited Lecture

9:10 AM - 9:30 AM JST | 12:10 AM - 12:30 AM UTC

[[A]D302-4am-01]

Control of the Assembly and Optical Properties of Halide Perovskite Nanomaterials

OTakuya Okamoto¹ (1. Hokkaido University)

◆ English ◆ Invited Lecture

9:30 AM - 9:50 AM JST | 12:30 AM - 12:50 AM UTC

[[A]D302-4am-02]

Ordered Arrangement of Semiconductor Nanocrystals using Supramolecular Polymer Templates

OMitsuaki Yamauchi¹ (1. Kyoto University)

► English ► Keynote Lecture

9:50 AM - 10:20 AM |ST | 12:50 AM - 1:20 AM UTC

[[A]D302-4am-03]

Short-Wave Infrared Emitting Halide Perovskites

OAngshuman Nag¹ (1. Indian Institute of Science Education and Research, Pune-411008, India)

► English ► Invited Lecture

10:20 AM - 10:40 AM JST | 1:20 AM - 1:40 AM UTC

[[A]D302-4am-04]

Organic Host Dispersion of Perovskite Nanocrystals via Aromatic Ligand Substitution

○Takayuki Chiba¹ (1. Yamagata University)

► English ► Invited Lecture

10:40 AM - 11:00 AM JST | 1:40 AM - 2:00 AM UTC

[[A]D302-4am-05]

Decomposition of Perfluoroalkyl Substances by Near-UV and Visible Light Irradiation to Semiconductor Nanocrystals

OYoichi Kobayashi^{1,2} (1. Ritsumeikan Univ., 2. PRESTO JST)

● English ● Keynote Lecture

11:00 AM - 11:30 AM JST | 2:00 AM - 2:30 AM UTC

[[A]D302-4am-06]

Nonclassical Behaviors in Early-Stage Crystallizations

OJungwon Park^{1,2} (1. Seoul National University, 2. Center for Nanoparticle Research, Institute for Basic Science (IBS))

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

Closing Remarks

© 2025 The Chemical Society of Japan

Control of the Assembly and Optical Properties of Halide Perovskite Nanomaterials

(¹ Research Institute for Electronic Science, Hokkaido University) OTakya Okamoto¹ **Keywords**: Perovskite; Quantum dot; Nanocrystal; Supercrystal; Photoluminescence

Halide perovskites show unique optical and electronic properties such as large absorption cross-section, size- and halide-dependent tunable bandgap, and excellent exciton and carrier transport properties. The excitonic and carrier recombination of perovskite nanomaterials can be modulated by assembly formation. However, the effects of the external stimuli-induced structural change of the perovskite nanomaterial assembly on their excitonic properties remain unexplored.

Here, we present the control of the assembly and optical properties in halide perovskite nanomaterials.¹⁻³ Firstly, we reported the control of the excitons and photoluminescence (PL) of self-assembled formamidinium lead bromide (FAPbBr₃) perovskite quantum dots (PQDs) under an applied mechanical force (Fig. 1a).¹ However, this mechano-optical modulation of the self-assembled PQDs is an irreversible process. To overcome this limitation, we demonstrated a heat-induced optical modulation of the PQD assembly in a polymer film (Fig. 1b).² On the other hand, the mechanical deforming of the highly ordered PQD assembly, known as supercrystals (PSCs), affects the long structural and optical stabilities. Finally, we demonstrated the formation of the slipping-free PSCs by the bidentate ligand exchange on cubic CsPbBr₃ PQDs (Fig. 1c).³ These studies provide new insights into controlling the optical properties of the perovskite nanomaterial assemblies, paving the way for advanced switchable optoelectronic device applications.

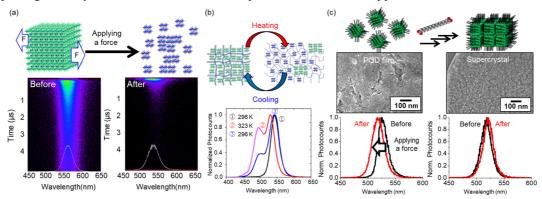


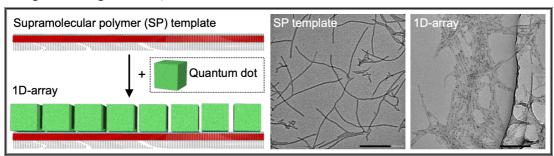
Fig. 1 (a) Mechanical force-induced optical property changes in the self-assembled PQDs. (b) Thermal modulation of excitonic recombination in the self-assembled PQDs in polymer films. (c) Slipping-free PSC formation using bidentate ligands.

1) Z. Zhang, S. Ghimire, T. Okamoto, B. M. Sachith, J. Sobhanan, C. Subrahmanyam, V. Biju, *ACS Nano*, **2022**, *16*, 160-168. 2) M. F. Khatun, T. Okamoto, V. Biju, *Chem. Commun.* **2023**, *59*, 13831-13834. 3) T. Okamoto, V. Biju, *Small*, **2023**, *19* (32), 2303496.

Ordered Arrangement of Semiconductor Nanocrystals using Supramolecular Polymer Templates

(Institute for Chemical Research, Kyoto University) ○Mitsuaki Yamauchi **Keywords**: Self-assembly; Semiconductor Nanocrystal; Supramolecular Polymer; Heterostructure; Transmission Electron Microscopy

Colloidal quantum dots (QDs) exhibit unique photophysical properties, including long-range energy diffusion, miniband formation, and collective photoluminescence, when aggregated into well-defined superstructures such as three- and two-dimensional superlattices. However, constructing one-dimensional (1D) QD superstructures, which feature a simpler arrangement, remains challenging. To address this, we have studied methods to control the self-assembly of QDs using supramolecular templates composed of organic dye molecules.^{1,2} Herein, we report a versatile strategy for forming 1D-arranged spherical QDs using a supramolecular polymer (SP) template.³ The templates consist of self-assembling cholesterol derivatives containing a hydrogen bonding moiety and an adhesion moiety that interacts with the QDs. When the SP and dispersed QDs are mixed in low-polarity solvents, the QDs adhere to the SP and self-arranged into 1D superstructures through van der Waals interactions between the organic ligands on the QD surface. This arrangement was confirmed by transmission electron microscopy. In-depth analyses of emission spectra and decay curves revealed efficient exciton energy transfer within the 1D-arranged QDs. Additionally, we report a novel SP template composed of naphthalenediimide derivatives for the formation of highly ordered cubic perovskite QDs.⁴ By turning the nanostructures of the SP template, we successfully controlled the arrangement range of the QDs.



- [1] M. Yamauchi*, S. Masuo, Chem.-Eur. J. 2019, 25, 167.
- [2] M. Yamauchi*, S. Yamamoto, S. Masuo*, Angew. Chem. Int. Ed. 2021, 60, 6473.
- [3] M. Yamauchi*, K. Nakatsukasa, N. Kubo, H. Yamada, S. Masuo*, *Angew. Chem. Int. Ed.* **2024**, *63*, e202314329.
- [4] A. M. Lena, M. Yamauchi*, H. Murakami, N. Kubo, S. Masuo, K. Matsuo, H. Hayashi, N. Aratani*, H. Yamada*, *Angew. Chem. Int. Ed.* **2025**, *in press*.

Short-Wave Infrared Emitting Halide Perovskites

Angshuman Nag

Department of Chemistry, Indian Institute of Science Education and Research (IISER), Pune 411008, India

E-mail: angshuman@iiserpune.ac.in

Short-wave infrared (SWIR) radiation, ranging from 700 to 1700 nm, is important for applications in bio-imaging, security camera, food inspection, remote-sensing, and optical fibre communication. Epitaxial grown III-V semiconductors are common choice for SWIR light emitting diodes (LEDs), but with limitations in mass production and high expense. Therefore, the development of suitable SWIR emitters, particularly the broadband ones, remains a significant challenge. This talk covers designing broadband SWIR emitters by doping metal halide double perovskites like Cs₂NaInCl₆. Such a host offers suitable octahedral coordination for potential SWIR-emitting dopants and is both stable and environmentally benign. Doping lanthanides such as Yb and Er produces sharp SWIR radiation at 990 nm and 1540 nm, respectively, via f-f transitions. 1,2 But the spectral width of f-f transitions is typically narrow. So, for achieving broadband SWIR emission, we doped transition metal ions with d-d transitions. Broad dual emitter covering white-light emission and SWIR emission was achieved by codoping Bi³⁺ and Cr³⁺. Thereafter, we achieved ultrabroad SWIR emitters with unprecedented FWHM of ~450 nm, by doping W⁴⁺ or Mo⁴⁺ in Cs₂Na_{0.95}Ag_{0.5}BiCl₆ double perovskite. Subsequently, we fabricated prototype phosphor-converted LED panels with over 100 LEDs, demonstrating their capabilities for SWIR imaging and food freshness inspection.

References:

- 1. Arfin, H.; Kaur, J.; Sheikh, T.; Chakraborty, S.; Nag, A. Bi³⁺-Er³⁺ and Bi³⁺-Yb³⁺ Codoped Cs₂AgInCl₆ Double Perovskite Near Infrared Emitters. *Angew. Chem. Int. Ed.* **2020**, *59*, 11307
- 2. Saikia, S.; Joshi, A.; Arfin, H.; Badola, S.; Saha, S; Nag, A. Sb³⁺–Er³⁺-Codoped Cs₂NaInCl₆ for Emitting Blue and Short-Wave Infrared Radiation. *Angew. Chem. Int. Ed.* **2022**, *61*, e20220162
- 3. Saikia, S.; Ghosh, A.; Nag, A. Broad Dual Emission by Codoping $Cr^{3+}(d \rightarrow d)$ and $Bi^{3+}(s \rightarrow p)$ in $Cs_2Ag_{0.6}Na_{0.4}InCl_6$ Double Perovskite. *Angew. Chem. Int. Ed.* **2023**, e202307689
- 4. Saikia, S.; Gopal, A.; Rathod, R.; Joshi, A.; Priolkar, K. R.; Saha, S.; Santra, P. K.; Shanmuganathan, K.; Nag, A. *Angew. Chem. Int. Ed.* **2025**, *64*, *e202415003*.

Organic Host Dispersion of Perovskite Nanocrystals via Aromatic Ligand Substitution

(¹ Graduate School of Organic Materials Science, Yamagata University)
○Takayuki Chiba¹

Keywords: Perovskite nanocrystals; Organic host dispersion; Aromatic ligand, LEDs

Metal halide perovskite nanocrystals (NCs) have recently attracted much attention for use in light-emitting devices (LEDs), given their high color purity and narrow full width at half maximum (FWHM) over the entire visible-wavelength range. ¹⁻⁶ The surface ligands of perovskite NCs capped with long alkyl chains play an important role in controlling the particle size during the synthesis and in achieving high colloidal stability in non-polar solvents. However, the long alkyl ligands, such as oleic acid (OA) and oleylamine (OAm), are generally insulating and thus reduce the electrical conductivity of the perovskite NC film, that is, the charge carrier injection and transport property, resulting in a higher driving voltage of the LEDs. Here, we demonstrate the aromatic ligand exchange of perovskite NCs to improve dispersibility in host organic materials. The aromatic ligand perovskite NCs enabled to form high quality composite film with small molecule host materials. The aromatic ligand NCs and small molecule host material composite achieved high photostability and operational device lifetime simultaneously.

- (1) S. Mizoguchi, S. Sumikoshi, H. Abe, Y. Ito, R. Yamakado, T. Chiba, Aromatic 2,2-diphenylethylamine ligand exchange of FA_{0.9}Cs_{0.1}PbBr₃ perovskite nanocrystals for high efficiency pure green light-emitting diodes, *ACS Omega* **2024**, 9, 34692–34699.
- (2) S. Ohisa, G. Motomura, S. Mizoguchi, Y. Fujisaki, T. Chiba, Ultra-Low Drive Voltage Perovskite Nanocrystal Light-Emitting Diodes Realized by an Auger Assisted Energy Up-Conversion, *Adv. Opt. Mater.* 2024, 2401456.
- (3) K. Satake, K. Narazaki, H. Abe, K. Yanagihashi, M. Mizukami, Y.i Suzuri, T. Chiba, J. Kido, Low-Temperature Annealing of Inkjet-Printed CsPbBr3 Perovskite Nanocrystal Film for Light-Emitting Diodes, *ACS Appl. Nano Mater.* **2024**, 7, 11313–11319.
- (4) H. Ebe, R. Suzuki, S. Sumikoshi, M. Uwano, R. Moriyama, D. Yokota, M. Otaki, K. Enomoto, T. Oto, T. Chiba, J. Kido, Guanidium Iodide Treatment of Size-controlled CsPbI₃ Quantum Dots for Stable Crystal Phase and Highly Efficient Red LEDs, *Chem. Eng. J.* 2023, 471, 144578.
- (5) F.-C. Liang, F.-C. Jhuang, Y.-H. Fang, J.-S. Benas, W.-C. Chen, Z.-L. Yan, W.-C. Lin, C.-J. Su, Y. Sato, T. Chiba, J. Kido, C.-C. Kuo*, Synergistic Effect of Cation Composition Engineering of Hybrid Cs_{1-x}FA_xPbBr₃ Nanocrystals for Self-Healing Electronics Application, *Adv. Mater.* 2023, 35, 2207617.
- (6) K. Satake, Y. Sato, K. Narazaki, T. Chiba, S. Sumikoshi, R. Moriyama, R. Suzuki, Y.-H. Cheng, K. Tamura, and J. Kido, Fabrication of perovskite nanocrystal light-emitting diodes via inkjet printing with high-temperature annealing, ACS Appl. Opt. Mater. 2023, 1, 282–288.

Decomposition of Perfluoroalkyl Substances by Near-UV and Visible Light Irradiation to Semiconductor Nanocrystals

(¹College of Life Sciences, Ritsumeikan University, ²PRESTO JST) ○Yoichi Kobayashi,¹,² **Keywords**: Nanocrystals; PFAS; Auger recombination; Up conversion

Perfluoroalkyl substances (PFASs) and fluorinated polymers (FPs) have been extensively utilized in various industries, whereas their extremely high stability poses significant challenges, such as environmental persistence and waste treatment. Current decomposition approaches of PFASs and FPs typically require harsh conditions such as heating over 400 °C. Thus, there is a pressing need to develop a new technique capable of decomposing them under mild conditions. Here, we showcase a method wherein perfluorooctanesulfonate, known as a "persistent chemical," and Nafion, a widely utilized sulfonated FP for ion-exchange membranes, undergo efficient decomposition into fluorine ions under ambient conditions via the irradiation of incoherent visible LED light onto semiconductor nanocrystals (NCs). This decomposition reaction is driven by cooperative mechanisms involving light-induced ligand displacements and Auger-induced electron injections via hydrated electrons and higher excited states. This study not only demonstrates the feasibility of efficiently breaking down various PFASs and FPs under mild conditions but also paves the way for advancing toward a sustainable fluorine-recycling society.

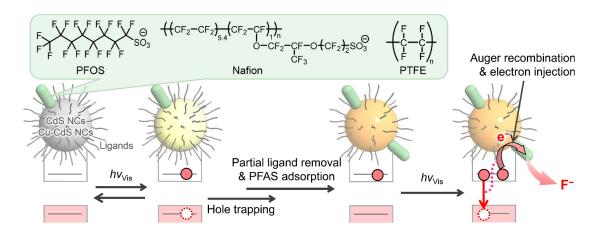


Figure 1. Plausible reaction mechanism of visible-light-induced defluorination of PFAS by semiconductor NCs.

1) Y. Arima, Y. Okayasu, D. Yoshioka, Y. Nagai, Y. Kobayashi, *Angew. Chem. Int. Ed.* **2024**, *63*, e202408687.

Nonclassical Behaviors in Early-Stage Crystallizations

(¹School of Chemical and Biological Engineering, Seoul National University, ²Center for Nanoparticle Research, Institute for Basic Science (IBS)) OJungwon Park, ^{1,2}

Keywords: Transmission Electron Microscopy; 3D Structure; Single Nanoparticle; Formation mechanism

Understanding the molecular and atomistic mechanisms underlying the synthesis, structure, and reactions of materials requires investigation at the nanoscale or below, a challenging task due to limited analytical methods capable of capturing in-situ structural information at such resolutions. Advanced in-situ transmission electron microscopy (TEM), including techniques like liquid-phase, electrochemical biasing, and cryo-TEM, offers unique opportunities to directly observe diverse chemical reactions at this scale.

In this talk, we present applications of in-situ TEM for studying nucleation, crystallization, and morphological transformations in various nanomaterials. Our findings reveal multiple non-classical pathways in material formation and crystallization, including two-step nucleation, amorphous-to-crystalline transitions, and cluster coalescence.

We also introduce a novel method combining liquid-phase TEM with computational reconstruction, enabling direct 3D atomic-scale structure mapping of single particles in solution.² This approach allows us to link atomic structures with the functional properties of nanomaterials. Furthermore, we demonstrate how electrochemical liquid-phase TEM provides insights into key interfacial reactions between heterogeneous catalysts and electrolytes.³ Real-time observations using liquid, gas, and cryo-TEM further extend these studies to electrode processes in various battery systems.

1) B. H. Kim et. al., Science **2020**, 368, 60. 2) S. Jeon et. al. Science **2021**, 371, 498. 3) S. Kim et. al. J. Am., Chem. Soc. **2025**, 147, 7804.