シンポジウム | アジア国際シンポジウム：アジア国際シンポジウム—ナノテク・材料化学ディビジョン/資源・エネルギー・地球化学・核化学・放射化学ディビジョン—

2024年3月20日(水) 9:00 ~ 11:40 A1422(14号館 [2階] 1422)

[A1422-3am] アジア国際シンポジウム—ナノテク・材料化学ディビジョン/資源・エネルギー・地球化学・核化学・放射化学ディビジョン—

座長、シンポジウム関係者：佐伯 昭紀、山方 啓、鳥本 司、白木 智丈

9:00 ~ 9:05

開会挨拶

英語 Invited Lecture

9:05 ~ 9:25

[A1422-3am-01]

ナノチューブ材料の化学修飾に基づく新規発光性ナノ材料の開発

〇白木 智丈[1,2] (1. 九大院工、2. 九大I2CNER)

日本語 Invited Lecture

9:25 ~ 9:45

[A1422-3am-02]

多元系量子ドットの高収率合成とマルチカラー発光

〇上松 太郎[1] (1. 大阪大学)

英語 Invited Lecture

9:45 ~ 10:05

[A1422-3am-03]

高効率・広帯域な光エネルギー変換を可能とする有機無機ハイブリッドマテリアルの創製

〇石井 あゆみ[1] (1. 早稲田大学)

10:05 ~ 10:20

休憩

英語 Keynote Lecture

10:20 ~ 10:50

[A1422-3am-04]

Revolutionizing Optoelectronics: Non-Fused Ring Electron Acceptors for Sustainability and Low-cost

〇Aung Ko Ko Kyaw[1] (1. Southern University of Science and Technology)

英語 Invited Lecture

10:50 ~ 11:10

[A1422-3am-05]

超耐久性を有する完全印刷プロセスによる多層多孔質電極型ペロブスカイト太陽電池

〇伊藤 省吾[1] (1. 兵庫県立大学)

英語 Keynote Lecture

11:10 ~ 11:40

[A1422-3am-06]

Insights and Advances in Copper(I) Thiocyanate: a Highly Versatile Coordination Polymer Semiconductor

○Pichaya Pattanasattayavong[1] (1. Vidyasirimedhi Institute of Science and Technology (VISTEC))

Molecular Functionalization of Nanotubes for Photoluminescent Nanomaterials Engineering

(*[1]Department of Applied Chemistry, Kyushu University, [2]International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University,*)
○Tomohiro Shiraki[1,2]

Keywords: Nanotubes, Chemical functionalization, Photoluminescence, Defect, Exciton

Nanotubes are one-dimensional nanomaterials with cylinder structures, exemplified by carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs). CNTs and BNNTs that have semiconducting features show excitonic photoluminescence (PL) in near-infrared and ultraviolet regions, respectively. Therefore, they are expected as photoluminescent nanomaterials applicable to advanced optical technologies including quantum light sources and biological nanosensors. Our strategy for nanotube functionalization is chemical modification,[1-3] in which covalent attachment of modifier molecules on the nanotube surfaces results in the defect formation via orbital hybridization conversion from sp^2 to sp^3 for the reacted atoms in their semiconducting crystalline structures. As a result, partial electronic structure changes occur, producing luminescent defects that show defect PL with enhanced functions such as bright and longer wavelength emissions (Figure 1).[4] Moreover, the molecular functions of the modified molecules including molecular recognition and photoisomerization can work as effective factors to change the bandgaps of the defect sites in the functionalized nanotubes, which allows to fabricate biological nanosensors[5] and a photoswitching system for the emission wavelengths.[6]

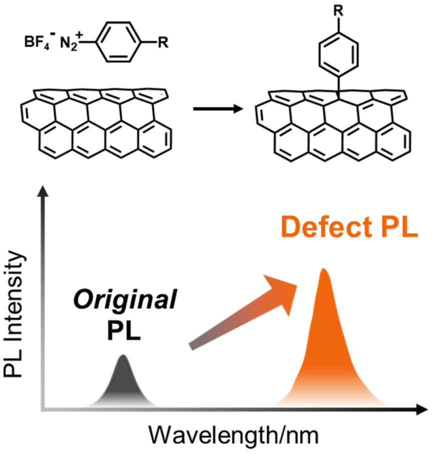

Figure 1. Schematic image of molecular functionalization of CNTs using diazonium chemistry (upper) and an observed PL spectral change (lower).

In this talk, our recent achievements regarding the molecularly functionalized nanotubes will be presented.

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High-yield Synthesis of Multinary Quantum Dots for Multicolor Emission

([1]*Graduate School of Engineering,* [2]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University*) ○Taro Uematsu[1,2]

Keywords: Cadmium-free, Multinary semiconductor quantum dots, Band-edge emission

Colloidal semiconductor quantum dots (QDs) are a new class of photoluminescent materials that exhibit monochromatic emission from band-edge transitions. The discovery of anomalous properties in nanosized semiconductors was made in the 1980s. In the following decade, QDs were developed into a practical photoluminescent material. This was supported by the invention of the hot injection method, a sophisticated organic approach to synthesize monodisperse inorganic crystals, and the development of the core/shell structure that allows surface passivation by larger bandgap inorganic materials. The 2023 Novel Prize was awarded to researchers who contributed to the discovery and development of QDs.

Since then, cadmium chalcogenide QDs, such as those made of CdS and CdSe, have been the focus of development. However, recent applications in display devices require cadmium-free alternatives. The most advanced alternative is InP QDs, but they have yet to reach the performance of Cd-based QDs. Multinary materials may also be candidates. Semiconductors composed of 11, 13, and 16 elements, represented by $CuInS_2$ and $AgInS_2$, exhibit band structures similar to those of CdSe. While the QDs of these materials exhibited relatively strong photoluminescence (PL), their spectral shape was significantly broader than that of Cd-based core/shell QDs due to intra-bandgap defect levels. In 2018, we reported the spectrally narrow band-edge emission in the yellow region (580 nm) by coating $AgInS_2$ QDs with a gallium sulfide (GaS_y) shell. [1]

Because $AgInS_2$ forms a wide range of solid solutions between elements of different periods, bandgap tuning by composition ratios is likely in addition to bandgap tuning by quantum size effects. For example, $AgInS_2$–$AgGaS_2$ solid solution has a larger bandgap than $AgInS_2$ and allows a blueshift of the band-edge PL (Figure 1).[2] However, the difficulty in synthesizing nanomaterials of quaternary composition has hindered the reproducible synthesis of $AgInS_2$–$AgGaS_2$ solid solution ($Ag(In_{1-x}Ga_x)S_2$) QDs. The difficulty stems from the different reactivity of the three metal precursors (Ag, In, and Ga) with an S source. This results in the overgrowth of Ag_2S nanoparticles, which eventually remains as a byproduct. In addition, the difference in reactivity between In and Ga sources causes inhomogeneity of composition and bandgap between the particles, which leads to the broadening of the PL spectrum.

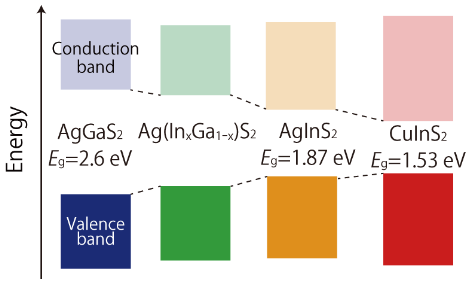

Figure 1. Bandgap tuning by solid-solution compositions of group 11, 13, 16 semiconductors.

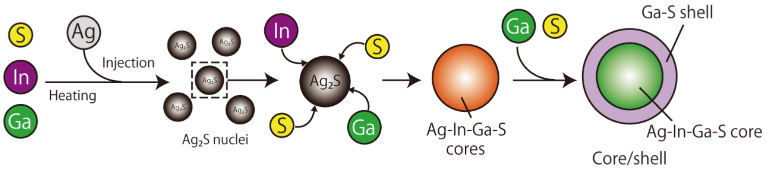

Figure 2. One-batch synthesis of quaternary QDs by injecting Ag source into the highly reactive sulfur source.

Figure 2 shows the new synthetic strategy to overcome the reactivity problem. Diethyldithiocarbamate was selected as an efficient source to produce metal sulfide and was introduced as a gallium complex. Silver acetate was injected into the heated solution containing Ga, In, and S sources. Due to the higher reactivity of Ag with S, Ag_2S nanoparticles were instantly generated. Although they should be prone to aggregation, the In, Ga, and S sources in the solution appeared to stabilize them. As the temperature increases, the In, Ga, and S sources are incorporated into the preformed Ag_2S nanoparticles and they are converted to the target $Ag(In_{1-x}Ga_x)S_2$ within a few minutes. A clear orange-red solution with an orange PL was obtained without any byproducts. Coating the $Ag(In_{1-x}Ga_x)S_2$ core QDs with the gallium sulfide shell allowed the generation of the band-edge PL in the green region, and the full width at half maximum was 30 nm, narrower than typical InP QDs (40 nm, Figure 3).[2]

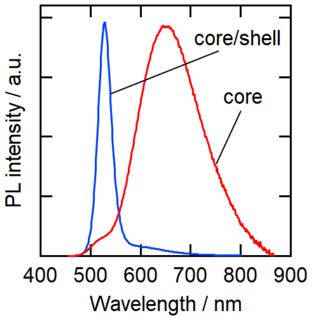

Figure 3. PL spectra of $Ag(In_{1-x}Ga_x)S_2$ core and $Ag(In_{1-x}Ga_x)S_2/GaS_y$ core/shell QDs.

The red emission was obtained by incorporating Cu into the $AgInS_2$ QDs, although the small amount of Ga is necessary for synthetic reasons (Figure 4). Unlike the green and yellow emission, the origin of the red emission was found to be a conduction band–Cu acceptor transition. This feature slightly broadens the PL spectral width (55 nm) even when compared in photon energy basis.[3] Nevertheless, red QDs comply with the ITU-R BT. 2020 standard for next-generation displays, and it is possible to achieve high color purity displays that meet 90% of this standard by using the green and red color QDs.

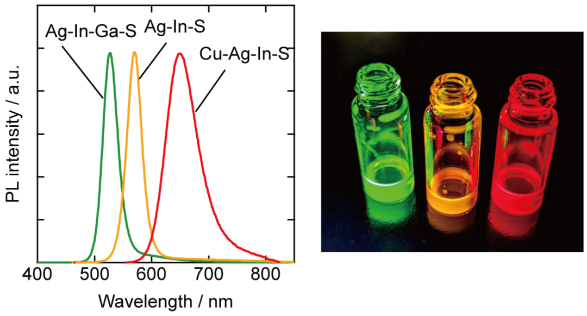

Figure 4. PL color tuning in wider range by compositional control including Cu.

1) T. Uematsu, K. Wajima, D. K. Sharma, S. Hirata, T. Yamamoto, T. Kameyama, M. Vacha, T. Torimoto, S. Kuwabata, *NPG Asia Mater.*, **2018**, *10*, 713. 2) T. Uematsu, M. Tepakidareekul, T. Hirano, T. Torimoto, S. Kuwabata, *Chem. Mater.*, **2023**, *35*, 1094. 3) T. Uematsu, N. Krobkrong, K. Asai, G. Motomura, Y. Fujisaki, T. Torimoto, S. Kuwabata, *Bull. Chem. Soc. Jpn.*, **2023**, *96*, 1274.

Development of Organic-Inorganic Hybrid Materials for Highly Efficient and Broad-band Photoenergy Conversion System

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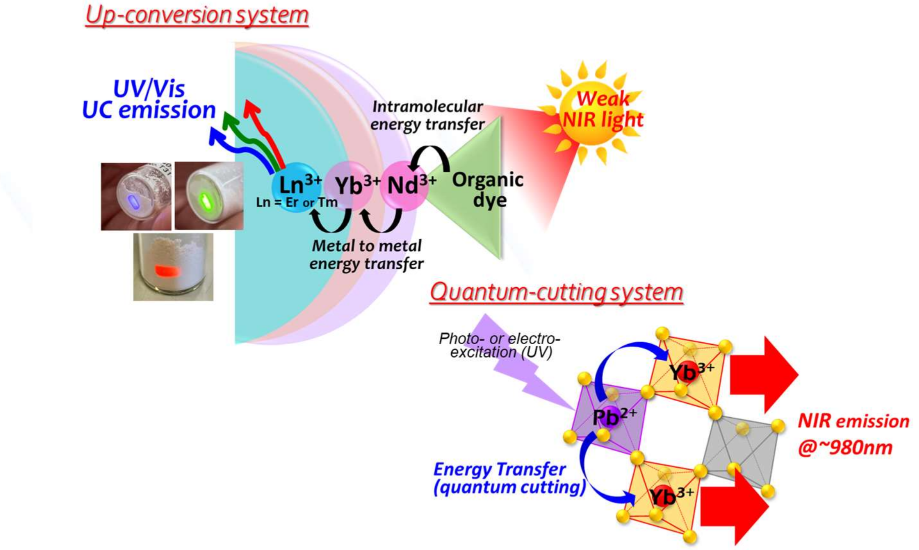
Keywords: Organic-inorganic hybrid; Photoenergy conversion; Near-infrared light; Up-conversion; Quantum cutting

Efficient light detection and utilization in the near-infrared (NIR) region are necessary in photoenergy conversion system such as solar cells, photodetectors, and photocatalytic systems. In this study, new NIR-sensitized systems using lanthanide-based hybrid nanomaterials, which show unique luminescence properties like up-conversion (UC) and quantum-cutting (QC), have been developed. For instance, dye-sensitized UC nanoparticles that can convert weak NIR light as sunlight into visible light with high efficiency were developed[1,2] and incorporated into a perovskite-based visible-light detector and solar cell[3,4]. The perovskite devices can detect broad-band solar light even in the NIR region through energy conversion from NIR to visible light in UC materials. And also, NIR light was sensitized as ultra-bright luminescence from Yb ion by using QC process, in which one-photon UV absorption of lead chloride-based perovskite nanocrystals is converted into two-photon NIR emission of Yb ions through the QC energy transfer[5,6]. The light-emitting diode was also fabricated and demonstrated 6% external conversion efficiency of field emission in the NIR region. The applications of the present study will lead to efficiency improvement in solar cells and photocatalysts by harvesting energy of NIR light in solar irradiation.



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Non-Fused Ring Electron Acceptors for Sustainable and Low-cost Optoelectronics

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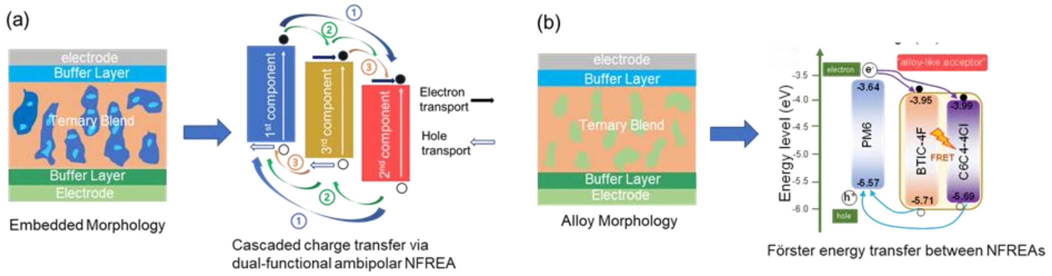
Keywords: Non-Fused Rring Electron Acceptor (NFREA); Organic Solar Cells; Ternary-Blend; Organic Photodetector

In recent years, the development of non-fullerene acceptors (NFAs) with ladder-type multiple fused ring structures has led to rapid advances in organic optoelectronic devices. However, the complex molecular architectures of fused ring electron acceptors require numerous synthetic and purification steps and hazardous substances, hindering large-scale synthesis and sustainability. Non-fused ring electron acceptors (NFREAs), on the other hand, offer several advantages such as simplified synthesis, facile chemical modifications, and straightforward tunability of optoelectronic properties. This talk will showcase A-π-A'-π-A structured NFREAs newly developed in our lab, their use in binary and ternary blend organic solar cells (OSCs)[1-2] and organic photodetector,[3] and how engineering of central core unit, alkyl chain, and terminal group influence device performance. The ambipolar NFREA,[4] alloy-like NFREA,[5] halogenation strategy in NFREA,[6] and their influence on ternary blend OSCs will be explained. Finally, I will discuss the synthesis complexity, cost analysis and figure-of-merit (FOM) values of NFREAs compared to traditional fused-ring type NFAs and explore the challenges and future directions of NFREAs for achieving high device performance and low production costs simultaneously.



Embedded Morphology

Cascaded charge transfer via dual-functional ambipolar NFREA

Alloy Morphology

Förster energy transfer between NFREAs

Figure 1. The ambipolar NFREA (a) and alloy-like NFREA (b) in ternary blend OSCs

References

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Fully-printed ultra-durable multi-porous-layered-electrode perovskite solar cells

(*Graduate School of Engineering, University of Hyogo*) ○Seigo Ito

Keywords: Perovskite Solar Cells; Porous Carbon Electrode; Stability

Commercialized photovoltaic panels need high stability against high temperature and strong radiation against sun illumination. Now, price of silicon solar modules is increasing due to the cease of Chinese government's budget. One of the candidates for next-generation photovoltaic panels against such tough circumstances is perovskite solar cells (PSCs), which have attracted the attention due to the high efficiency and the cost-effective manufacturing by printing system. Organo-lead halide perovskite crystal ($CH_3NH_3PbI_3$ is the most studied perovskite crystal) can work for the light-absorbing and carrier-transporting material as a semiconductor. The photoenergy conversion efficiency (*Eff.*) has been improved from 3.8% at 2008 to 25.7% at present, by additives mixed in the precursor solution of $CH_3NH_3PbI_3$. However, PSCs have not been stable against circumstances, because the organo-lead halide perovskite crystal ($CH_3NH_3PbI_3$) reacts with water and changes to PbI_2, and because the iodide (I^-) reacts with the back contact metal (Au or Ag), resulting in the deterioration of *Eff.* To solve these two problems, porous-carbon-electrodes have been introduced in PSCs, which have multi-porous-layered electrodes of TiO_2, ZrO_2 and carbon. The perovskite precursor ($(HOOC(CH_2)_4NH_3)_{0.05}(CH_3NH_3)_{0.95}PbI_3$ in GBL) is deposited through porous electrodes of TiO_2, ZrO_2 and carbon, resulting in multi-porous-layered electrode perovskite solar cells (MPLE-PSCs). The conductivity of carbon electrodes can't be deteriorated by iodide (I^-) in the organo-lead halide perovskite crystal. Moreover, the porous-carbon electrode filled with the perovskite crystal can block the penetration of water. Although the best *Eff.* of MPLE-PSC is 18.8%, the MPLE-PSCs show very high stability as,

1) Thermal stability at 100 ℃ over 4500 h in dark (by Univ. of Hyogo, Japan).
2) Damp-heat stability at 85 ℃-85%RH over 3,000 h in dark (by Univ. of Hyogo and Kishu Giken Kogyo, Japan).
3) Light stability at 55 ℃ over 10,000 h (by EPFL, Switzerland).

In the conference, challenging works of high thermal stability over 100 ℃ are presented. Such high temperature is required for outer space application.

Insights and Advances in Copper(I) Thiocyanate: a Highly Versatile Coordination Polymer Semiconductor

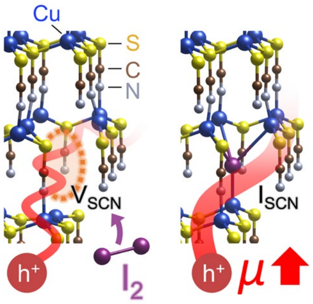
([1]*Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand*) ○Pichaya Pattanasattayavong[1]

Keywords: Copper(I) thiocyanate; p-Type Semiconductors; Coordination Polymers; Hole Transport; Electronic Devices

Coordination polymers are an expansive class of materials with a rich variety of structures and properties. Recently, the interest in exploiting their electronic and optoelectronic properties for device applications has begun to emerge;[1] however, most examples are specific device configurations and limited applicability. From the field of organic and oxide electronics, copper(I) thiocyanate (CuSCN) has been consistently demonstrated as an excellent hole-transport material (HTM) with a wide range of applications from thin-film transistors (TFTs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), perovskite solar cells (PSCs), as well as photodetectors and sensors among others. [2–4]

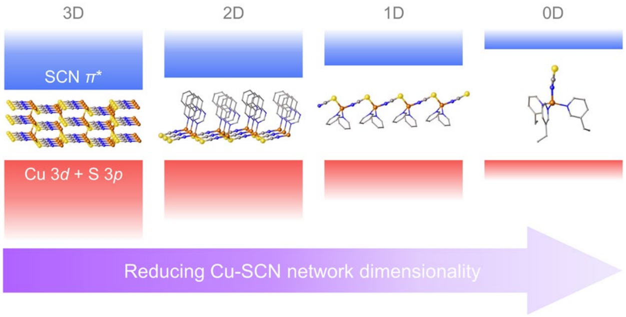
The unique attributes of CuSCN that allow its extensive applications lie in the electronic structure and solution-processability. The electronic bands of CuSCN comprise a Cu 3d-dominant valence band (with some S 3p hybridization) and a SCN π^* conduction band. This results in dispersed hole-transporting states, yielding high hole mobility on the order of 0.01 to 0.1 $cm^2\ V^{-1}\ s^{-1}$, and a high-energy conduction band level, giving rise to a large band gap of >3.5 eV and an excellent electron-blocking ability.[5] These properties are ideal for the HTM in devices. Moreover, CuSCN can be formed as compact thin films using common solution-based deposition methods. The latter further allows it to be incorporated in a wide range of devices as mentioned.

Despite the exciting advances in the device applications, the fundamental knowledge about the structure-property relationship of CuSCN is still lacking. For example, the coordination chemistry aspect of CuSCN in device-relevant conditions is unexplored despite its direct influence on the device performance. CuSCN is typically processed with sulfur- or nitrogen-containing solvents because these soft donor groups can interact with the soft Cu(I) acceptor. Recently, we showed that such interactions play an important role on the nanoscale morphology of CuSCN films and crystallinity. Treating CuSCN films with antisolvents, such as tetrahydrofuran (THF), can improve film quality and subsequently device characteristics.[6] Furthermore, the solvent molecules are 'sticky' (remain in the film during deposition), and their removal can lead to SCN^- vacancies, which are defect states that adversely affect the hole-transport properties. To this end, we showed that iodine can be used to passivate the defects, restore the coordination environment around Cu(I), and also improve the device performance.[7]



(Figure shows the passivation of SCN$^-$ vacancy defect by I$^-$ substitution.)

Exploring the coordination chemistry of CuSCN further, its structure and the crucial Cu-S network can be modified by carefully selecting the co-ligands. The starting 3D structure can be reshaped into 2D, 1D or 0D depending on the number and steric hindrance of co-ligands. Using aromatic co-ligands can also bring about interesting effects, such as optical absorptions and emissions in the visible spectrum or the possibility of charge transport through the co-ligand sub-substructure.[8] CuSCN is fascinating in that it provides a platform for the study of structure-property-device performance that can be expanded to other coordination polymers and open up this class of materials for the electronic and optoelectronic device applications.



(Figure shows the changes in the structure and electronic band levels in CuSCN due to co-ligand modifications.)

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