

Academic Program [Oral A] | 21. Energy and Related Chemistry, Geo and Space Chemistry : Oral A

📅 Thu. Mar 27, 2025 1:00 PM - 3:40 PM JST | Thu. Mar 27, 2025 4:00 AM - 6:40 AM UTC 🏛️  
[A]A405(A405, Bldg. 1, Area 3 [4F])

## **[[A]A405-2pm] 21. Energy and Related Chemistry, Geo and Space Chemistry**

Chair: Hideki Tanaka, Tomokazu Umeyama

◆ Japanese

1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC

[[A]A405-2pm-01]

Bond Cleavage Effect of 2D-Extended A' Core in A-D-A'-D-A Type Non-Fullerene Acceptor for Organic Photovoltaic Devices

○Kenta Yamada<sup>1</sup>, Wataru Suzuki<sup>1</sup>, Tomokazu Umeyama<sup>1</sup> (1. UNIVERSITY OF HYOGO)

◆ Japanese

1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC

[[A]A405-2pm-02]

Optical Spin Device Functions of Pb(II)/Bi(III)/Te(IV)-based 1D Helical Perovskite Thin Films

○Hikari Suzuki<sup>1</sup>, Daiki Nakamura<sup>1</sup>, Yusuke Kinoshita<sup>1</sup>, Ayumi Ishii<sup>1</sup> (1. School of Advanced Science and Engineering, Waseda University)

◆ Japanese

1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC

[[A]A405-2pm-03]

Near-infrared wavelength-selective organic solar cells with a p-i-n structure using tin(IV) 2,3-naphthalocyanine dichloride

○Tomonori Imamura<sup>1</sup>, Naoya Aizawa<sup>1</sup>, Mitsuharu Suzuki<sup>1</sup>, Ken-ichi Nakayama<sup>1</sup> (1. The University of Osaka)

◆ Japanese

1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC

[[A]A405-2pm-04]

Effect of Copper Dithione Complexes-Based Redox Shuttles on Photovoltaic Performances of Dye-Sensitized Solar Cells

○Hiroshi Higuchi<sup>1</sup>, Tomohiro Higashino<sup>1</sup>, Hiroshi Imahori<sup>1,2,3</sup> (1. Grad. Sch. Eng., Kyoto Univ., 2. WPI-iCeMS, Kyoto Univ., 3. ILAS, Kyoto Univ.)

◆ Japanese

1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC

[[A]A405-2pm-05]

Influence of Atmospheric Fabricating Conditions on Performance for P3HT:Nonfullerene Acceptor-based Organic Solar Cells

○Naoya Tagashira<sup>1</sup>, Shreyam Chatterjee<sup>1</sup>, Yutaka Ie<sup>1,2</sup> (1. SANKEN, Osaka Univ., 2. ICS-OTRI, Osaka Univ.)

◆ Japanese

1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC

[[A]A405-2pm-06]

Stabilization of complex dyes using Cross-linked ionic Liquid-Modified TiO<sub>2</sub> substrates in dye-sensitized solar cells.

○Arata Nishizawa<sup>1</sup> (1. Graduate school of engineering, Nagoya institute of technology)

---

◆ Japanese

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

[[A]A405-2pm-07]

Tuning the Photochemical Properties of AgGaSe<sub>2</sub> Quantum Dots through Chemical Composition Control

○Haruka Asai<sup>1</sup>, Kazutaka Akiyoshi<sup>1</sup>, Tatsuya Kameyama<sup>1</sup>, Taro Uematsu<sup>2</sup>, Tsukasa Torimoto<sup>1</sup> (1. Nagoya University, 2. Osaka University)

---

◆ English

2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

[[A]A405-2pm-08]

Photocurrent Enhancement of Bi<sub>2</sub>Se<sub>3</sub> Quantum Dot Modified-TiO<sub>2</sub> Nanotube Array by Au Nanoparticle

○Kazuki Inoue<sup>1</sup>, Abouelela Mohamed Marwa<sup>2</sup>, Wai Kian Tan<sup>1</sup>, Hiroyuki Muto<sup>1</sup>, Atsunori Matsuda<sup>1</sup>, Go Kawamura<sup>1</sup> (1. Toyohashi University of Technology, 2. Egyptian Petroleum Research Institute)

---

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

Break

---

◆ English

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[[A]A405-2pm-09]

Fabrication of an Ionic Thermoelectric Generator using Carbon Nanotube Electrodes

○Jiaxu Zhao<sup>1,2</sup>, Naoki Tanaka<sup>3,4</sup>, Tsuyohiko Fujigaya<sup>3,4,5</sup> (1. Fukuoka International School, 2. Kyushu Univ. QFC-SP, 3. Grad. Sch. Eng., Kyushu Univ., 4. WPI-I2CNER, 5. Kyushu Univ. Center for Molecular Systems (CMS))

---

◆ Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[[A]A405-2pm-10]

Effect of cold pressing and aging on thermoelectric properties of Ag<sub>2</sub>Se nanowire thin films

○Kurumi Kubota<sup>1</sup>, Haruna Kasugai<sup>1</sup>, Shunya Sakane<sup>2</sup>, Hideki Tanaka<sup>1</sup> (1. Chuo University, 2. Ibaraki University)

---

◆ English

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[[A]A405-2pm-11]

Liquid Cooling by Electrochemical Peltier Cell Combining Acid-Base Responsive Polymer Nanoparticles and Proton-Coupled Electron Transfer Reaction

○Ryuto Iwata<sup>1</sup>, Yusuke Wakayama<sup>1</sup>, Hongyao Zhou<sup>1</sup>, Teppei Yamada<sup>1</sup> (1. The University of Tokyo)

---

◆ Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[[A]A405-2pm-12]

Synthesis and thermoelectric performance evaluation of  $\alpha$ -Cu<sub>2</sub>Se nanowires/reduced graphene oxide flexible films

○Ryuhei Mita<sup>1</sup>, Tatsuki Miura, Syunya Sakane<sup>2</sup>, Hideki Tanaka<sup>1</sup>, Yuto Hatanaka<sup>1</sup> (1. The Univ. of Chuo, 2. The Univ. of Ibaraki)

---

🇯🇵 Japanese

3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC

[[A]A405-2pm-13]

Enhanced thermoelectric performance in PEDOT:PSS/titanium dioxide mixed thin films by UV irradiation

○TAKUMI SAKAMOTO<sup>1</sup>, Takuto Touyama, Akito Ayukawa<sup>2</sup>, Shunya Sakane<sup>2</sup>, Hideki Tanaka<sup>1</sup> (1. The Univ. of Chuo, 2. The Univ. of Ibaraki)

---

🇯🇵 Japanese

3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC

[[A]A405-2pm-14]

Development of Energy Storage Devices Using Solid Electrolyte Interphase (SEI) Charge Storage

○Taichi Kida<sup>1</sup>, Minako Deguchi<sup>1</sup>, Masashi Ishikawa<sup>1</sup> (1. kansai university)

---

🇯🇵 Japanese

3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC

[[A]A405-2pm-15]

Surface Treatment of LATP-based Oxide Solid Electrolytes for Use with Li metal Electrodes and Application to Composite Solid Electrolytes

○Komei Sawada<sup>1</sup>, Gen Hassegawa<sup>2</sup>, Naoaki Kuwata<sup>2</sup>, Masashi Ishikawa<sup>1</sup> (1. Kansai university, 2. National Institute for Materials Science)

---

## 有機薄膜太陽電池素子応用を志向した A-D-A'-D-A 型非フラーレンアクセプターにおける 2 次元拡張 A' コアの結合切断効果

(兵庫県大院工) ○山田 健太・鈴木 航・梅山 有和

Bond Cleavage Effect of 2D-Extended A' Core in A-D-A'-D-A Type Non-Fullerene Acceptor for Organic Photovoltaic Devices (*Graduate School of Engineering, University of Hyogo*)

○Kenta Yamada, Wataru Suzuki, Tomokazu Umeyama

We prepared novel acceptor-donor-acceptor'-donor-acceptor (A-D-A'-D-A) type non-fused ring electron acceptors, CRIC and BRIC, both of which have a quinoxaline (Qx) derivative as the central A' unit. Phenanthrene is fused to the Qx ring in BRIC, whereas the 4a-4b bond of the fused phenanthrene is cleaved in CRIC. This bond cleavage at 4a-4b had an insignificant impact on optical properties and energy levels. However, CRIC exhibited a considerably lower aggregation tendency compared to BRIC, attributed to the moderate intermolecular interactions in CRIC, as revealed by  $^1\text{H}$  NMR spectra at various concentrations. In blend films with a conjugated polymer donor PBDB-T, photoluminescence (PL) quenching was more efficient for CRIC (95%) than for BRIC (90%), suggesting more effective exciton diffusion to the donor-acceptor interface in PBDB-T:CRIC due to smaller domain sizes. As a result, the CRIC-based organic photovoltaic (OPV) device exhibited a higher short-circuit current density ( $20.3\text{ mA cm}^{-2}$ ), resulting in a superior power conversion efficiency (11.6%), compared to the BRIC-based device ( $17.2\text{ mA cm}^{-2}$  and 8.2%, respectively).

**Keywords :** Nonfullerene Acceptor; Quinoxaline; Organic Photovoltaics; Bond Cleavage Effect; Exciton Diffusion Efficiency

電子不足コアユニットとしてキノキサリン誘導体を用いた新規 A-D-A'-D-A 型非縮環型電子アクセプター (NFREA) である CRIC と BRIC を合成した (Figure 1a)。BRIC ではキノキサリンに対してフェナントレンが縮環されており、CRIC ではその 4a-4b 結合が切断されている。両者の溶液および薄膜での光学特性、エネルギー準位には大きな違いが見られなかった。しかし、濃度依存  $^1\text{H}$  NMR 測定の結果から、高濃度のクロロホルム溶液中で、BRIC は凝集体を形成するが、CRIC では凝集体形成は起こらないことがわかった。共役系高分子ドナーである PBDB-T との複合薄膜を作成したところ、PBDB-T:CRIC の方が PBDB-T:BRIC よりも表面の凹凸が小さいことが、原子間力顕微鏡測定よりわかった。また複合薄膜と NFREA 単膜の発光強度を比較したところ、CRIC の消光率 (95%) は BRIC (90%) よりも高かった。これらの結果から、CRIC は複合膜において適切なドメインサイズを達成し、生成した励起子がドナー:アクセプター界面に到達する効率が向上したと考えられる。そのため、複合薄膜を光活性層とした有機薄膜太陽電池 (OPV) 素子の評価を行ったところ (Figure 1b)、CRIC を用いた素子において短絡電流密度が大きくなり、変換効率が高くなった (CRIC: 11.6%、BRIC: 8.2%)。

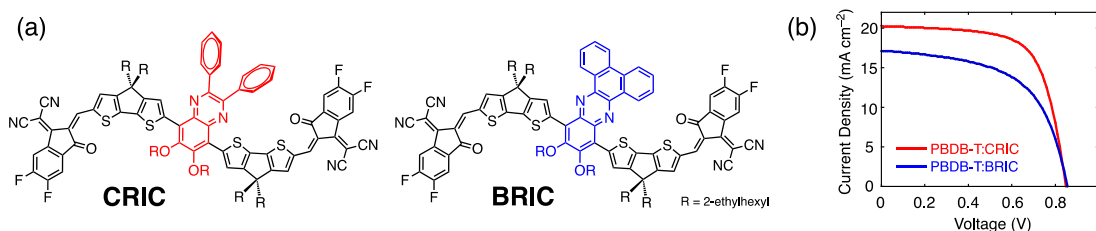


Figure 1. (a) Structures of CRIC and BRIC. (b)  $J$ - $V$  characteristics of OPV devices.

## Pb(II)/Bi(III)/Te(IV)を用いた一次元らせんペロブスカイト薄膜の光スピndeバイス機能

(早大先進理工<sup>1)</sup>) ○鈴木 ひかり<sup>1</sup>・中村 大輝<sup>1</sup>・木下 雄介<sup>1</sup>・石井 あゆみ<sup>1</sup>  
 Optical Spin Device Functions of Pb(II)/Bi(III)/Te(IV)-based 1D Helical Perovskite Thin Films  
 (<sup>1</sup>*School of Advanced Science and Engineering, Waseda University*)  
 ○Hikari Suzuki,<sup>1</sup> Daiki Nakamura,<sup>1</sup> Yusuke Kinoshita,<sup>1</sup> Ayumi Ishii<sup>1</sup>

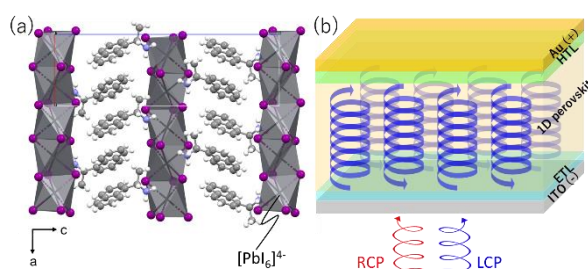
We have developed a thin-film device with a one-dimensional (1D) helical structure composed of an organic chiral molecule and lead halide, achieving direct detection of circularly polarized light (CPL) in the UV region. In this study, we fabricated 1D helical thin films incorporating heavy atoms to control the optical and electrical properties arising from broken spatial inversion symmetry and spin interactions. The 1D helical thin films in which Pb(II) was replaced with Bi(III) or Te(IV) exhibited selective absorption of CPL in the visible region.

**Keywords :** One-dimensional helical structure; Halide perovskite; Circularly polarized light; Organic-inorganic hybrid; Spin

円偏光や直線偏光の検出は、物体の複屈折や応力を可視化する技術として近年高い注目を集めている。これまでに本研究では、有機キラル分子とハロゲン化鉛からなる一次元らせん構造の薄膜デバイスを構築し、紫外領域の円偏光の直接検出に成功している<sup>1)</sup>。本系の特異的な円偏光検出特性は、構造全体のキラリティ（空間反転対称性の破れ）と大きなスピン軌道相互作用に由来すると考えられる。本研究では、空間反転対称性が破れた構造とスピンの寄与する光・電气的特性の制御を目的とし、種々の重原子（Pb(II)、Bi(III)、Te(IV)）を用いた一次元らせん薄膜を作製し、その光デバイス機能を検証した。

有機キラル分子には、*R*-(+)-および *S*-(-)-(1-ナフチル)エチルアミン (*R*- or *S*-NEA<sup>+</sup>)を用い、PbI<sub>2</sub>、BiI<sub>3</sub>、または、TeI<sub>4</sub>と共にジメチルホルムアミドに溶解させて前駆体溶液とし、スピンコート法により導電性基板上に結晶薄膜を形成した。PbI<sub>2</sub>は *R*(*S*)-NEA<sup>+</sup>との反応により、[PbI<sub>6</sub>]<sup>4-</sup>からなる八面体ユニットが面共有で連結した一次元らせん構造 ((*R*- or *S*-NEA)PbI<sub>3</sub>)を形成する (Fig. 1a)。この結晶薄膜は、キララルな空間群 *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>であり、400 nm に 5000 mdeg (*g*<sub>CD</sub>=0.08) を超える強い円偏光二色性 (CD) を示す。この CD 吸収は、主に *I*5p 軌道から *Pb*6p 軌道への間接遷移に対応する。*Pb*(II)の代わりに *Bi*(III)および *Te*(IV)を用いることで、CD 吸収帯は可視光領域に移行した。これらの一次元らせん薄膜を用いたデバイス (Fig. 1b) は、CD 吸収帯に対応する円偏光照射により電流応答を示し、紫外から可視光領域における円偏光検出を達成した。

1) A. Ishii, T. Miyasaka, *Science Adv.* **2020**, 6, eabd3274.



**Fig. 1** (a) Single crystal structure of (*S*-NEA)PbI<sub>3</sub> and (b) the photoelectric conversion device.

## スズ(IV)ナフタロシアニンジクロリドを用いた近赤外波長選択型 p-i-n 有機太陽電池

(阪大院工<sup>1)</sup>) ○今村 友宣<sup>1</sup>・相澤 直矢<sup>1</sup>・鈴木 充朗<sup>1</sup>・中山 健一<sup>1</sup>

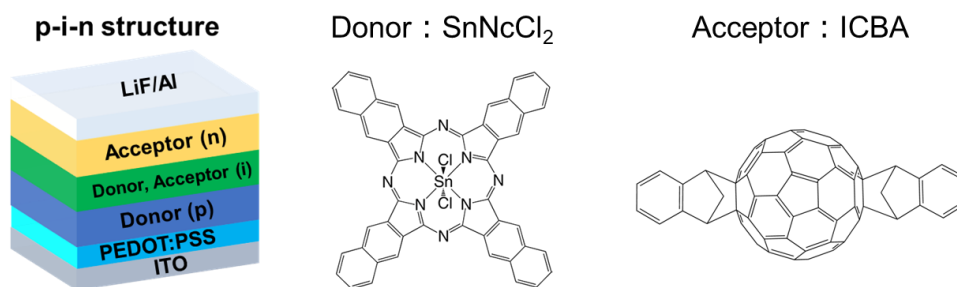
Near-infrared wavelength-selective organic solar cells with a p-i-n structure using tin(IV) 2,3-naphthalocyanine dichloride (<sup>1</sup>*Graduate School of Engineering, Osaka University*)

○Tomonori Imamura,<sup>1</sup> Naoya Aizawa,<sup>1</sup> Mitsuharu Suzuki,<sup>1</sup> Ken-ichi Nakayama<sup>1</sup>

Organic solar cells (OSCs) have great potential for being lightweight, flexible, and wavelength-selective absorption;<sup>1)</sup> in particular, OSCs with selective sensitivity in the near-infrared (NIR) region are suitable for agrivoltaics and transparent solar cells. In recent years, many attempts have been reported to extend absorption into the NIR region in bulk heterojunction OSCs, but it remains challenging to realise transparent OSCs in the visible region with high sensitivity in the NIR region. In this study, we fabricated NIR wavelength-selective OSCs with a p-i-n structure using tin(IV) 2,3-naphthalocyanine dichloride with a broad absorption band in the NIR region, and the acceptor ICBA with low visible absorption. The device achieved high internal quantum efficiency exceeding 50% in 800–1000 nm. Furthermore, a semitransparent device with dielectric layers was fabricated.

**Keywords :** Organic Solar Cell; Tin(IV) 2,3-naphthalocyanine dichloride; Near-infrared Absorption; Transparent Solar Cell

有機太陽電池(OSC)は、軽量・フレキシブルのほか、吸収波長を自在に調節できるという利点があり<sup>1)</sup>、特に近赤外波長選択型太陽電池は、営農型発電や透明太陽電池の実現のために重要である。近年、バルクヘテロ型 OSC において近赤外領域まで吸収波長を拡張する試みが数多く報告されているが、可視域の吸収を抑え、かつ近赤外領域で高い感度をもつ OSC の報告例は少ない。そこで本研究では、ドナーとして近赤外領域で幅広い吸収を持つスズ(IV)ナフタロシアニンジクロリド、アクセプターとして可視域の吸収が小さい ICBA を組み合わせた、p-i-n 構造近赤外波長選択型太陽電池を作製したところ、800~1000 nm において内部量子効率 50%以上が得られた。さらに、誘電体層を導入した半透明太陽電池を作製した。



1) S. Jinnai, et al., *ACS Sustainable Chem. Eng.*, **11**, 1548 (2023).

## 銅ジチオン錯体レドックス対を用いた色素増感太陽電池におけるジチオン配位子構造の効果

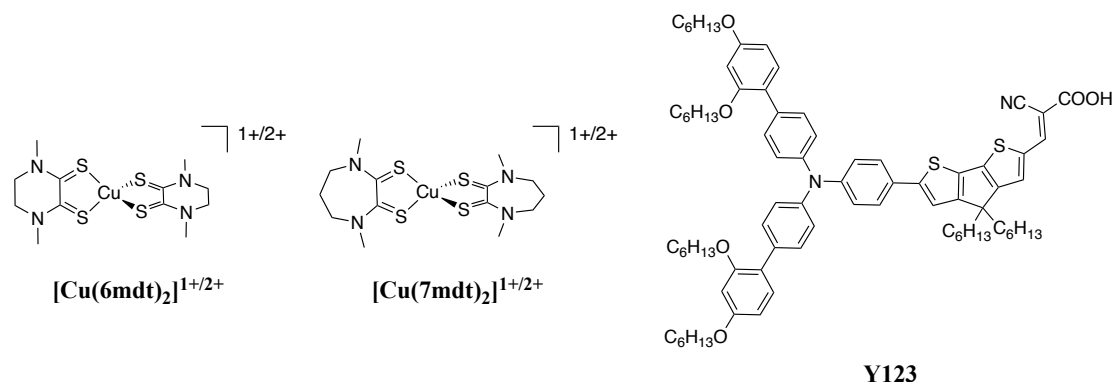
(京大院工<sup>1</sup>・京大 WPI-iCeMS<sup>2</sup>・京大 ILAS<sup>3</sup>) ○樋口 寛<sup>1</sup>・東野 智洋<sup>1</sup>・今堀 博<sup>1,2,3</sup>

Effect of Copper Dithione Complexes-Based Redox Shuttles on Photovoltaic Performances of Dye-Sensitized Solar Cells (<sup>1</sup>*Graduate School of Engineering, Kyoto University*, <sup>2</sup>*WPI-iCeMS, Kyoto University*, <sup>3</sup>*ILAS, Kyoto University*) ○ Hiroshi Higuchi,<sup>1</sup> Tomohiro Higashino,<sup>1</sup> Hiroshi Imahori<sup>1,2,3</sup>

Dye-sensitized solar cells (DSSCs) with copper redox shuttles have attracted considerable attention due to their ability to achieve high open circuit voltage and resultant high power conversion efficiency, attributed to their more positive redox potential. Recently, DSSCs utilizing copper dithione complexes as redox shuttles have demonstrated power conversion efficiencies comparable to those employing copper bipyridyl complexes. In this study, we designed and synthesized copper dithione complexes and evaluated the photovoltaic performances of Y123-based DSSCs.

**Keywords :** dye-sensitized solar cells; copper; dithione ligands; redox shuttles

近年、色素増感太陽電池のレドックス対として銅錯体が注目されている。これまで、主に銅ビピリジル錯体などの窒素原子を配位原子とする錯体を用いることで、開放電圧の向上と高いエネルギー変換効率が実現されてきた。一方で最近、硫黄原子を配位原子とする銅ジチオン錯体を用いることで銅ビピリジル錯体と同等のエネルギー変換効率を達成できることが報告されている<sup>1)</sup>。しかしながら、銅ジチオン錯体の配位子構造が太陽電池性能に与える影響は未だ不明である。そこで本研究では、新たな銅ジチオン錯体を合成し、色素 **Y123** と組み合わせた色素増感太陽電池を作製し、太陽電池性能評価を行った。その結果、7員環骨格をもつ配位子をもつ錯体 ( $[\text{Cu}(\text{7mdt})_2]^{1+/2+}$ ) を用いた場合、6員環骨格をもつ配位子をもつ錯体 ( $[\text{Cu}(\text{6mdt})_2]^{1+/2+}$ ) と比較し、エネルギー変換効率が向上することを見出した。本講演では、その詳細について発表する。



1) Yang, X. et al. *ACS Appl. Energy Mater.* **2021**, 4, 14004.

## P3HT：非フラーレンアクセプター型有機太陽電池の大気下での作製環境が性能に及ぼす影響

(阪大産研<sup>1</sup>・阪大 ICS-OTRI<sup>2</sup>) ○田頭 直也<sup>1</sup>・Chatterjee Shreyam<sup>1</sup>・家 裕隆<sup>1,2</sup>

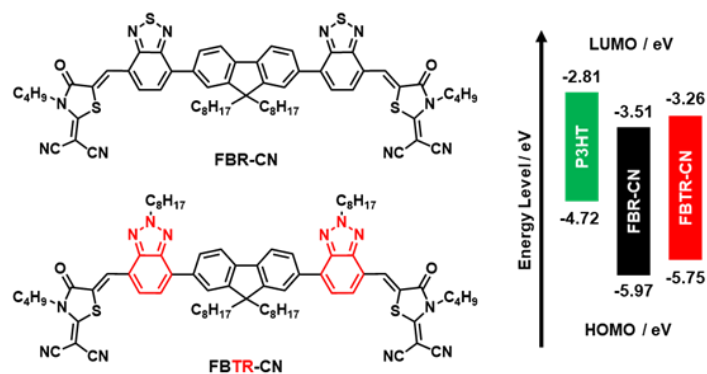
Influence of Atmospheric Fabricating Conditions on Performance for P3HT:Nonfullerene Acceptor-based Organic Solar Cells (<sup>1</sup>SANKEN, Osaka University, <sup>2</sup>ICS-OTRI, Osaka University) ○Naoya Tagashira,<sup>1</sup> Chatterjee Shreyam,<sup>1</sup> Yutaka Ie<sup>1,2</sup>

Organic solar cells (OSCs) are attracting attention as a next-generation energy source. Large-area OSCs aimed for social implementation should be fabricated under atmospheric conditions, but the power generation efficiency of OSC is lower than that of fabricated under inert atmosphere. In this study, we designed and synthesized FBR-CN, and prepared OSCs using nonfullerene acceptors (FBR-CN and FBTR-CN) and poly(3-hexylthiophene) to investigate the effect of the fabrication atmosphere on the OSC performance. We also investigated the effect of a fullerene derivative (PC<sub>61</sub>BM) as an additive under atmospheric conditions.

**Keywords :** Organic Solar Cells; Nonfullerene Acceptors; Atmospheric Fabrication; Green-light Wavelength Selectivity; Poly(3-hexylthiophene)

有機太陽電池 (OSCs) は次世代の再生可能エネルギー源として注目されている。大面積の OSC モジュールは大気条件下で作製されるが、不活性条件下で作製した場合と比較して発電効率 (PCE) が低下することが社会実装に向けた課題となっている。本研究では、発電層材料のエネルギー準位が大気条件下での PCE 低下に及ぼす影響を検討するために、代表的なドナーポリマーの poly(3-hexylthiophene) (P3HT) 向けアクセプター材料である

FBR-CN<sup>1</sup>に着目し、FBR-CNと比較して浅い最低空軌道エネルギー準位を有するFBTR-CNを設計・合成し、OSCの作製条件が太陽電池性能に及ぼす影響を検討した(右図)。また、発電層へのフラーレン誘導体(PC<sub>61</sub>BM)の添加が大気条件下での作製に及ぼす影響に関しても検討を行った。<sup>2</sup>



**Figure.** Chemical structures of nonfullerene acceptors used in this study and their energy levels.

- 1) S. Chatterjee, Y. Iimuro, Y. Watanabe, Y. Ie, *J. Photopolym. Sci. Technol.*, **2024**, 37, 191.
- 2) E. Trippodo, V. Campisciano, L. W. Feng, Y. Chen, W. Huang, J. M. Alzola, D. Zheng, V. K. Sangwan, M. C. Hersam, M. R. Wasielewski, B. Pignataro, F. Giacalone, T. J. Marks, A. Facchetti, *J. Mater. Chem. C*, **2023**, 11, 8074.



## 色素増感型太陽電池における架橋型イオン液体修飾 TiO<sub>2</sub> 電極を用いた錯体色素の安定化

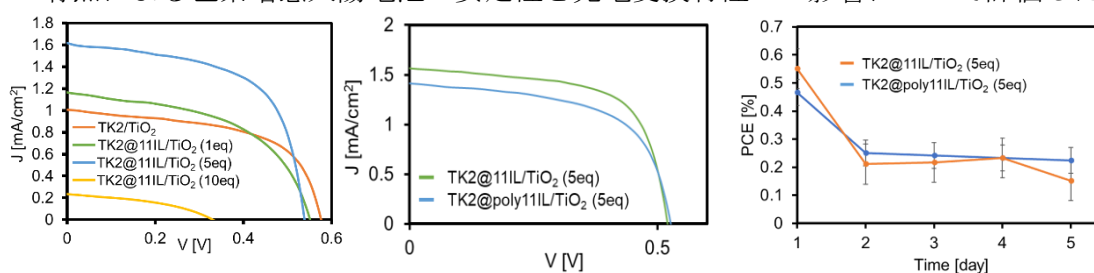
(名工大院工<sup>1</sup>・愛工大院工<sup>2</sup>) ○西澤新太<sup>1</sup>・倉橋那成<sup>1</sup>・北川竜也<sup>1</sup>・猪股智彦<sup>1</sup>、小澤智宏<sup>1</sup>、増田秀樹<sup>2</sup>

Improvement of stability and durability of sensitized dyes using cross-linked ionic liquid-modified TiO<sub>2</sub> substrates in dye-sensitized solar cells. (<sup>1</sup>Graduate School of Engineering, Nagoya Institute of Technology, <sup>2</sup>Graduate School of Engineering, Aichi Institute of Technology) ○Nishizawa Arata,<sup>1</sup> Tomonari Kurahashi,<sup>1</sup> Tatsuya Kitagawa,<sup>1</sup> Tomohiko Inomata,<sup>1</sup> Tomohiro Ozawa,<sup>1</sup> Hideki Masuda<sup>2</sup>

We have found that the photoelectric conversion efficiency of dye-sensitized solar cells can be increased by using electrodes with sensitized dyes immobilized on ionic liquid-modified TiO<sub>2</sub> substrates. In this study, we synthesized ionic liquids with terminal cross-linking groups and prepared their modified TiO<sub>2</sub> electrodes with copper complex dyes. We evaluated the effects of cross-linking on the stability of Cu complex dyes and photoelectric conversion properties.

**Keywords :** Dye sensitized solar cell, Ionic liquid, Cross linking, Copper complex dye

色素増感太陽電池 (DSSC) は、設計の容易さや低コストから次世代太陽電池として注目されているが、不安定性や光電変換効率の低さが課題である。我々はこれまでにイオン液体 (IL) を修飾した電極を利用した研究を行っているが<sup>1-3</sup>、イオン液体修飾チタニア電極を色素増感太陽電池に利用した場合、色素の凝集および逆電子移動反応を抑制し、その変換効率が大きく上昇することを報告している<sup>4</sup>。本研究では、末端に架橋基を有するイオン液体修飾 TiO<sub>2</sub> 電極を用い、それらと不安定な銅錯体色素を用いて色素増感太陽電池を作製した。**Figure 1** に示したようにイオン液体間の架橋の有無による色素増感太陽電池の安定性と光電変換特性への影響について評価した。



**Figure 1.** (Left) The I-V plots of DSSCs based on IL-modified TiO<sub>2</sub> electrode and Cu complex dye (TK2), the differences of (Middle) the I-V plots and (Right) the stabilities for the DSSCs before and after polymerization of ILs on the TiO<sub>2</sub> electrode.

1) T. Kitagawa, *et al.*, *Chem. Commun.*, **2013**, 49, 10184-10186; 2) T. Kitagawa, *et al.*, *Chem. Lett.*, **2016**, 45, 436-438; 3) T. Kitagawa, *et al.*, *Chem. Commun.*, **2016**, 52, 4780-4783; 4) T. Inomata, *et al.*, *RSC Adv.*, **2022**, 12, 19624-19630;

組成制御による AgGaSe<sub>2</sub> 量子ドットの光化学特性の変調

(名大院工<sup>1</sup>・阪大院工<sup>2</sup>) ○浅井 晴香<sup>1</sup>・秋吉 一孝<sup>1</sup>・亀山 達矢<sup>1</sup>・上松 太郎<sup>2</sup>・鳥本 司<sup>1</sup>

Tuning the Photochemical Properties of AgGaSe<sub>2</sub> Quantum Dots through Chemical Composition Control

(<sup>1</sup>Nagoya Univ., <sup>2</sup>Osaka Univ.) ○Haruka Asai,<sup>1</sup> Kazutaka Akiyoshi,<sup>1</sup> Tatsuya Kameyama,<sup>1</sup> Taro Uematsu,<sup>2</sup> Tsukasa Torimoto<sup>1</sup>

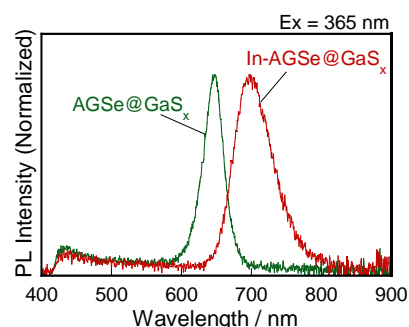
Quantum dots (QDs) composed of multinary semiconductors exhibit unique optical properties that can be tuned by adjusting their particle size and chemical composition. These characteristics have made them the subject of extensive research aimed at developing novel photofunctional materials. In this paper, we report the liquid-phase synthesis of low-toxicity AgGaSe<sub>2</sub> (AGSe) QDs. These QDs were synthesized by reacting suitable metal precursors and selenium compounds in a hot organic solvent. The resulting QDs were surface-coated with GaS<sub>x</sub>, resulting in the appearance of a sharp emission peak around 650 nm. Furthermore, doping AGSe QDs with In<sup>3+</sup> induced a red shift of the emission peak to ca. 710 nm.

**Keywords :** *Quantum Dot; Less-toxicity semiconductor; Chalcopyrite structure; Core-shell structure; Photoluminescence*

低毒性な多元半導体量子ドットは、粒子のサイズや化学組成に依存した光学特性を示すため、ディスプレイの発光材料や生体イメージング材料などへの応用が期待されている。これまでに我々は、可視光領域の約 450 nm にシャープな発光ピークを示す AgGaS<sub>2</sub> 量子ドットを作製することに成功した<sup>(1)</sup>。本研究では、より広範囲な波長領域で発光特性を制御するために、AgGaSe<sub>2</sub>(AGSe)量子ドットに着目し、その液相合成法を開発した。さらに得られた量子ドットに In<sup>3+</sup>をドーピングし、その発光波長の制御を試みた。

AGSe 量子ドットは、AgOAc、Ga(acac)<sub>3</sub>、セレンウレアをオレイルアミン (OLA) と 1-ドデカンチオールとの混合溶媒中で 300 °C で 10 分間加熱することにより合成した。この量子ドットを Ga(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub> および GaCl<sub>3</sub> とともに OLA 中で加熱し、GaS<sub>x</sub> シェルで表面を被覆して AGSe@GaS<sub>x</sub> コアシェル構造粒子を得た。

Ag/Ga=0.4 の前駆体比を用いて合成した AGSe 量子ドットは発光を示さなかったが、Fig. 1 に示すように、GaS<sub>x</sub> シェルで被覆することで 650 nm 付近にシャープなバンド端発光ピークを示した。その半値幅は 34 nm となり、CdSe などの高毒性元素を持つ二元量子ドットに近い値を示した。さらに、AGSe 量子ドットを In(acac)<sub>3</sub> と含む OLA 中で 250 °C で加熱することで粒子表面に In<sup>3+</sup>をドーピングすると (In-AGSe)、GaS<sub>x</sub> シェル被覆後の量子ドット (In-AGSe@GaS<sub>x</sub>) の発光ピークが、710 nm に長波長シフトした。このことは、AGSe 量子ドット表面と GaS<sub>x</sub> シェル層の間に、エネルギーギャップのより小さい Ag(In,Ga)Se<sub>2</sub> 半導体層が形成されたためである。



**Fig. 1.** PL spectra of AGSe@GaS<sub>x</sub> and In-AGSe@GaS<sub>x</sub> QDs.

(1) T. Tozawa *et al.*, *ACS Appl. Mater. Interfaces* **2024**, *16*, 68169.

## Photocurrent Enhancement of Bi<sub>2</sub>Se<sub>3</sub> Quantum Dot Modified TiO<sub>2</sub> Nanotube Array by Au Nanoparticle

(<sup>1</sup>Toyohashi University of Technology, <sup>2</sup>Egyptian Petroleum Research Institute) ○Kazuki, Inoue<sup>1</sup>, Marwa, Abouelela<sup>2</sup>, Wai Kian, Tan<sup>1</sup>, Hiroyuki, Muto<sup>1</sup>, Atsunori, Matsuda<sup>1</sup>, Go, Kawamura<sup>1</sup>

**Keywords:** photoelectrochemical reaction, plasmon resonance, solar hydrogen generation

TiO<sub>2</sub> nanotube array (TNTA) is a promising photoelectrode material component for photoelectrochemical hydrogen generation<sup>1)</sup>. To achieve efficient solar light utilization, it is essential to harness visible light, which accounts for about 52 % of sunlight. Although surface modification with narrow-bandgap chalcogenide quantum dots (QDs) has been studied for the use of visible light, their light absorbance is insufficient<sup>2)</sup>. Plasmonic metal nanoparticles (NPs) can enhance photocurrents of PEC systems through localized surface plasmon resonance (LSPR), which generates a strong oscillating electric field near the NPs that efficiently excites electrons in nearby semiconductors.

In this research, we fabricated Bi<sub>2</sub>Se<sub>3</sub> QDs-decorated TNTA photoelectrode, coupled with plasmonic Au NPs serving as light-harvesting antennae (Fig. 1a and 1b). We observed that the photocurrent enhancement depended on the Bi<sub>2</sub>Se<sub>3</sub> decoration conditions, with SILAR method of 2 cycles showed the highest enhancement (Fig. 1c). The SEM/EDX analysis indicated an increase in both quantity and size of QDs with the number of SILAR cycles. An increase in their quantity contributed to absorption improvement; however, the photocurrent was decreased when the SILAR cycle increased to be 4. The decrease in photocurrent was attributed to the quenching effect via energy transfer from QDs to plasmonic NPs<sup>3)</sup>. The optimization of Au NPs deposition conditions was also carried out to further enhance the photocurrent performance.

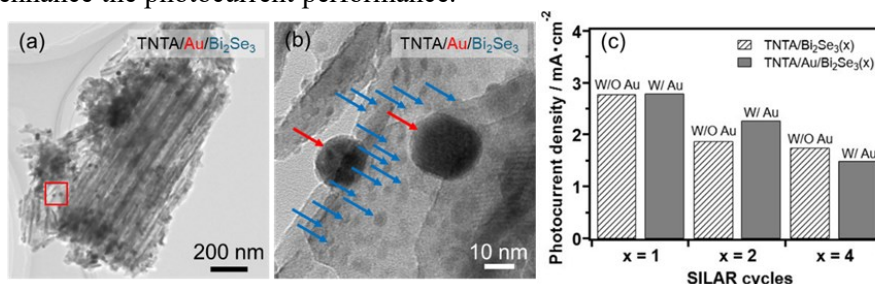


Figure 1. (a) TEM image of TNTA/Au/Bi<sub>2</sub>Se<sub>3</sub>. (b) Magnified image of the red squared area in (a). The red and blue arrows indicate Au NPs and Bi<sub>2</sub>Se<sub>3</sub> QDs, respectively. (c) Photocurrent density of TNTA/Bi<sub>2</sub>Se<sub>3</sub> with/without Au NPs, as a function of the number of SILAR cycles.

1) K. Inoue, G. Kawamura et. al., *Sci Rep* **2023** 13, 103. 2) M.M. Abouelela, K. Inoue, G. Kawamura et al., *SM&T* **2023** 38, e00718. 3) T. Kawawaki et al., *Phys. Chem. Chem. Phys.* **2013**, 15, 20247-20251.

## カーボンナノチューブ電極を用いたイオン熱電変換素子の開発

(福岡インターナショナルスクール<sup>1</sup>・九大 QFC-SP<sup>2</sup>・九大院工<sup>3</sup>・I<sub>2</sub>CNER<sup>4</sup>・九大 CMS<sup>5</sup>)○趙 佳旭<sup>1,2</sup> 田中 直樹<sup>3,4</sup> 藤ヶ谷 剛彦<sup>3,4,5</sup>

Fabrication of an Ionic Thermoelectric Generator using Carbon Nanotube Electrodes (<sup>1</sup>Fukuoka International School, <sup>2</sup>QFC-SP, Kyushu Univ., <sup>3</sup>Grad. Sch. Eng., Kyushu Univ., <sup>4</sup>I<sub>2</sub>CNER, <sup>5</sup>Center for Molecular Systems (CMS)) ○Jiaxu Zhao<sup>1,2</sup>, Naoki Tanaka<sup>3,4</sup>, Tsuyohiko Fujigaya<sup>3,4,5</sup>

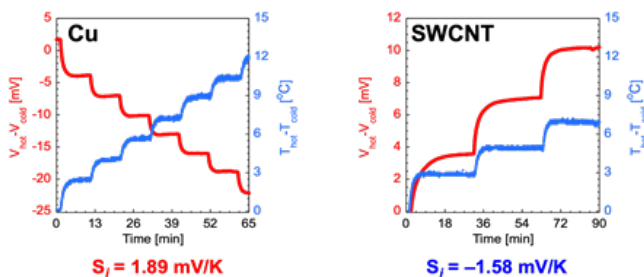
Thermoelectric generators (TEGs) generate electricity from temperature differences and are promising for applications in flexible electronics. Among them, ionic thermoelectric generators (i-TEGs), which use ion diffusion, have a high electromotive force and can be utilized as thermoelectric capacitors. In this research, the use of carbon nanotube (CNT) sheets as electrodes was studied, with an emphasis on their excellent mechanical flexibility. To measure the potential difference generated, CNT sheets were placed at both ends of a polymer electrolyte composed of polyvinyl alcohol (PVA) containing potassium chloride (KCl), and a temperature gradient was introduced. An ionic Seebeck coefficient of approximately 1.0 ~ 2.0 mV/K was achieved. Interestingly, while copper electrodes exhibited p-type character, the CNT sheets showed n-type character. This suggests that the interaction between CNTs and the electrolyte significantly differs from that of copper electrodes.

**Keywords:** Ionic Thermoelectric Generators, Ionic Seebeck Effect, Carbon Nanotubes, Polymer electrolytes

温度差で発電する熱電変換デバイスは、利便性を高めたフレキシブルデバイスへの応用が期待されている。その中でも、イオンの拡散を利用したイオン型熱電発電デバイス (i-TEG) は、熱起電力が高く、熱電キャパシタとしての応用が可能である [1]。そこで本研究では、従来検討されてきた金属電極に加え、柔軟性に優れる単層カーボンナノチューブ (SWCNT) 膜を電極に用いることを検討した。

熱起電力測定にはポリビニルアルコール (PVA) に塩化カリウム (KCl) を加えた高分子電解質の両端に SWCNT 膜を貼り付け、温度差を加えたところ、約 1.0~2.0 mV/K ほどのイオンゼーベック係数が得られた (Fig. 1)。興味深いことに、銅を電極として用いた場合においては温度差上昇に対して低温側の電位が上昇する p 型を示すのに対し、SWCNT を電極とした場合はその逆の挙動を示す n 型であった。これは SWCNT と電解質間の相互作用が、銅電極の場合とは異なるために生じたと考えしている。

[1] Y. He *et al.*, *J. Phys. Chem. Lett.* **2022**, *13*, 4621–4627.



**Fig. 1.** Thermoelectric voltage response over time for i-TEGs using (left) Cu and (right) SWCNT electrodes and a PVA-KCl polymer electrolyte under varying temperature differences.

## Ag<sub>2</sub>Se ナノワイヤ薄膜の熱電特性におけるコールドプレス条件の影響

(中央院理工<sup>1</sup>・中央理工<sup>2</sup>茨大院理工<sup>3</sup>) ○久保田くるみ<sup>1</sup>、春日井陽菜<sup>1</sup>、坂根駿也<sup>3</sup>、田中秀樹<sup>1,2</sup>)

Effect of cold pressing and aging on thermoelectric properties of Ag<sub>2</sub>Se nanowire thin films (<sup>1</sup>Graduate School of Science and Engineering, Chuo University, <sup>2</sup>Faculty of Science and Engineering, Chuo University, <sup>3</sup> Faculty of Science and Engineering, Ibaraki University Graduate School) ○Kurumi Kubota<sup>1</sup>, Haruna Kasugai<sup>1</sup>, Shunya Sakane<sup>3</sup>, Hideki Tanaka<sup>1,2</sup>

Thermoelectric materials are capable of directly converting heat into electricity, and their performance is evaluated by power factor ( $S^2\sigma$ ) using Seebeck coefficient ( $S$ ) and electrical conductivity  $\sigma$ . So far, we have successfully synthesized Ag<sub>2</sub>Se nanowires, a thermoelectric material, by photoreduction method. In this study, we investigated thin film processing methods to improve the strength of flexible films with Ag<sub>2</sub>Se nanowires. Ag<sub>2</sub>Se nanowires films were fabricated by suction filtration. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) were used for structural characterization. TE properties were evaluated by measuring  $S$  and  $\sigma$  using a homemade device and the van der Pauw method, respectively. The thin films were cold-pressed after suction filtration to increase the strength of the surface while maintaining their flexibility. In addition, the density of nanowires increased in the thin film after cold pressing, resulting in an improvement of  $\sigma$ . The increased strength of the thin films allowed repeated measurements of thermoelectric properties, and changes in performance over time could be investigated.

*Keywords: Thermoelectric materials, Silver selenide, Nanowires, Conductive polymer, Photoreduction, Cold-pressed*

熱電材料は熱を電気に直接変換することのできる材料であり、その性能はゼーベック係数  $S$ 、電気伝導率  $\sigma$  を用いて出力因子 ( $S^2\sigma$ ) で評価される。これまで我々は、光還元法により熱電材料である Ag<sub>2</sub>Se ナノワイヤの合成に成功してきた。本研究では、Ag<sub>2</sub>Se ナノワイヤを用いて作製したフレキシブル膜の加工方法を検討し、強度を向上することを目的とした。Ag<sub>2</sub>Se ナノワイヤ膜は吸引ろ過で作製した。構造評価は、X 線回折法(XRD)、走査型電子顕微鏡(SEM)、エネルギー分散型 X 線分析(EDX)を行った。物性評価は、自作装置による  $S$  の測定と、van der Pauw 法にて  $\sigma$  の測定を行った。薄膜は、成膜後のコールドプレスによって柔軟性を維持しながら表面の強度を高めることに成功した。また、コールドプレス後の薄膜では、ナノワイヤの密度が上昇し、 $\sigma$  の向上が確認された。薄膜の強度向上によって熱電特性の繰り返しの測定が可能となり、熱電特性の経過時間依存性を測定できた。

## Liquid Cooling by Electrochemical Peltier Cell Combining Acid–Base Responsive Polymer Nanoparticles and Proton-Coupled Electron Transfer Reaction

(School of Science, Department of Chemistry, the University of Tokyo)

○Ryuto Iwata, Yusuke Wakayama, Hongyao Zhou, Teppei Yamada

keywords: electrochemical Peltier effect, Proton-coupled electron transfer, LCST phase transition, Polymer nanoparticle, NIPAM

Liquid cooling by electrochemical Peltier (ECP) effect is expected to be an alternative cooling technology, because this method can achieve active heat transportation, which has been a problem in solid-state Peltier cooling. In the previous research<sup>[1]</sup>, a redox-active and thermo-responsive polymer was used for the ECP cooling and achieved 0.5 mK depression. One problem of this system is slow diffusion of the polymer in solution. Herein we aimed to solve this problem by using Brayton cycle combining acid–base responsive polymer and proton-coupled electron transfer (PCET) reaction, anticipating that the diffusion rate can be increased by using the PCET-active molecules. The PCET-active molecules mixed acid–base-responsive polymer show a large positive or negative Seebeck coefficient ( $S_e$ )<sup>[2]</sup>. The acid-responsive and the base-responsive polymers are separated by a semipermeable membrane (Figure 1a).

Poly(acrylic acid-*co*-N-isopropylacrylamide) (AAc NPs) and poly(N,N-dimethylaminopropyl methacrylamide-*co*-N-isopropyl-acrylamide) (DAPM NPs) were respectively used as the acid-responsive and the base-responsive polymers. Quinhydrone (QH) was used as the PCET-active redox pair. QH mixed with AAc NPs showed a negative  $S_e$  value, while the same redox pair mixed with DAPM NPs showed a positive  $S_e$  value (Figure 1b). The ECP cell composed of QH and AAc NPs showed  $\Delta T_{\max}$  of 3.2 mK, which is larger than the cell without NPs (Figure 1c). In contrast, the  $\Delta T_{\max}$  was decreased by the addition of DAPM NPs, likely because the  $S_e$  is shifted toward a positive value by DAPM NPs. These results indicate that the change of  $S_e$  values of the PCET-active redox pair by acid–base-responsive polymers is reflected on the value of  $\Delta T_{\max}$ . This study shows the possibility that acid–base responsive polymers and PCET-active redox pairs can be integrated into Brayton cycle.

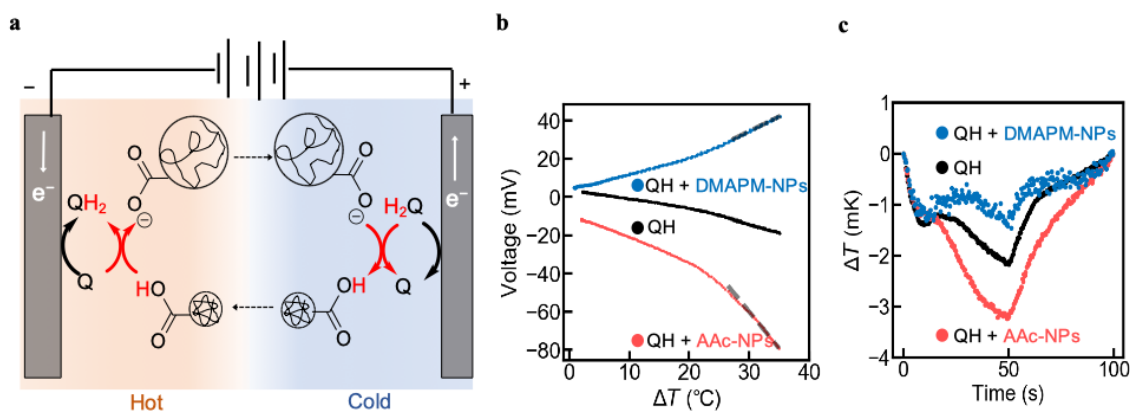


Figure 1. a) Schematic image of ECP cell. b) Seebeck coefficient c) ECP effect in a static cell

[1] Zhou, H., Matoba, F., Matsuno, R., Wakayama, Y., & Yamada, T., *Advanced Materials* **2023**, 35(36). [2] Guo, B., Hoshino, Y., Gao, F., Hayashi, K., Miura, Y., Kimizuka, N., & Yamada, T., *J. Am. Chem.* **2020**, 142(41), 17318–17322.



## $\alpha$ -Cu<sub>2</sub>Se ナノワイヤ/還元型酸化グラフェンフレキシブル膜の合成 および熱電性能評価

(中央院理工<sup>1</sup>・中央理工<sup>2</sup>茨大院理工<sup>3</sup>) ○三田竜平<sup>1</sup>、三浦達樹、畑中勇人<sup>2</sup>、坂根駿也<sup>3</sup>、田中秀樹<sup>1,2</sup>

Synthesis and thermoelectric performance of  $\alpha$ -Cu<sub>2</sub>Se nanowire/reduced graphene oxide flexible films (<sup>1</sup>Graduate School of Science and Engineering, Chuo University, <sup>2</sup>Faculty of Science and Engineering, Chuo University, <sup>3</sup> Faculty of Science and Engineering, Ibaraki University Graduate School) ○Ryuhei Mita<sup>1</sup>, Tatsuki Miura, Yuto Hatanaka<sup>2</sup>, Shunya Sakane<sup>3</sup>, Hideki Tanaka<sup>1,2</sup>

Thermoelectric(TE) materials are materials that can directly convert heat into electricity, and their performance is expressed by the power factor  $S^2\sigma$ , which is determined by the Seebeck coefficient  $S$  and electrical conductivity  $\sigma$ . Carbon-based materials, which are rich in elements and have low toxicity, have attracted attention as clean thermoelectric materials. Reduced graphene oxide (rGO) in particular shows excellent flexibility and high electrical conductivity, but its low thermoelectric performance is considered to be an issue. We have demonstrated that hybridization with inorganic materials is effective in improving thermoelectric performance.<sup>[1]</sup> The purpose of this study was to improve the thermoelectric performance by mixing rGO with  $\alpha$ -Cu<sub>2</sub>Se nanowires (NWs), which have high performance at room temperature. The powders of rGO and  $\alpha$ -Cu<sub>2</sub>Se NWs were dispersed in ethanol, and the solution was suction filtered to prepare a flexible film. The content of  $\alpha$ -Cu<sub>2</sub>Se NWs was changed and the performance was compared. The structure was evaluated by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray analysis (EDX), and Raman spectroscopy. For physical property evaluation, the Seebeck coefficient was measured using a homemade device, and the electrical conductivity was measured using the van der Pauw method.

As a result, TE performance tended to improve as the content of  $\alpha$ -Cu<sub>2</sub>Se NWs increased.

**Keywords :** Thermoelectric materials, Copper selenide, Nanowire, Reduced graphene oxide, Photoreduction

熱電材料とは熱を電気に直接変換できる材料であり、その性能はゼーベック係数  $S$  と電気伝導率  $\sigma$  を用いた出力因子  $S^2\sigma$  で表される。元素が豊富で毒性の低い炭素系材料は、クリーンな熱電材料として注目されている。還元型酸化グラフェン(rGO)は優れた柔軟性と高い導電性を示すが、熱電性能が低いことが課題とされている。我々はこうした熱電性能の高度化にあたり、無機材料と混合するハイブリッド化が有効であることを明らかにしてきた。<sup>[1]</sup>本研究は、rGO に室温で高い性能を持つ  $\alpha$ -Cu<sub>2</sub>Se ナノワイヤ(NW)を混合し、熱電性能を向上させることを目的とした。rGO と  $\alpha$ -Cu<sub>2</sub>Se NWs の粉末をエタノール中に分散し、その溶液を吸引ろ過することでフレキシブル膜を作製した。この時  $\alpha$ -Cu<sub>2</sub>Se NWs の含有量を変え、性能の比較を行った。構造評価は X 線回折法(XRD)、走査型電子顕微鏡(SEM)、エネルギー分散型 X 線分析(EDX)、ラマン分光法を行った。物性評価は自作装置によりゼーベック係数を、van der pauw 法により電気伝導率を測定した。

結果として、 $\alpha$ -Cu<sub>2</sub>Se NWs の含有量を増やすほど熱電性能が向上する傾向が見られた。  
1) Syunya Sakane, *et al.* ACS Omega **2022**, 7, 32101–32107

## PEDOT:PSS/酸化チタン混合薄膜における紫外光照射による熱電性能向上

(中央院理工<sup>1</sup>・中央理工<sup>2</sup> 茨大院理工<sup>3</sup>) ○坂本拓巳<sup>1</sup>、東山拓杜<sup>1</sup>、鮎川瞭仁<sup>3</sup>、坂根駿也<sup>3</sup>、田中秀樹<sup>1,2</sup>

Enhanced thermoelectric performance in PEDOT:PSS/titanium dioxide mixed thin films by UV irradiation. (<sup>1</sup>Graduate School of Science and Engineering, Chuo University, <sup>2</sup>Faculty of Science and Engineering, Chuo University, <sup>3</sup> Faculty of Science and Engineering, Ibaraki University Graduate School) ○Takumi Sakamoto<sup>1</sup>, Takuto Toyama<sup>1</sup>, Akito Ayukawa<sup>3</sup>, Shunya Sakane<sup>3</sup>, Hideki Tanaka<sup>1,2</sup>

Thermoelectric (TE) materials can convert heat into electricity directly, and their performance is evaluated by power factor ( $S^2\sigma$ ), using Seebeck coefficient  $S$  and electrical conductivity  $\sigma$ . The organic TE material PEDOT:PSS has a low thermal conductivity  $\kappa$  and excellent flexibility which are properties advantageous for TE materials, but its performance is still low. Titanium dioxide ( $\text{TiO}_2$ ) has the property of emitting electrons by UV light irradiation<sup>[1]</sup>. Therefore, in this study, PEDOT:PSS was mixed with  $\text{TiO}_2$  and irradiated with UV light to improve its TE performance. The mixed solution was spin-coated and annealed on glass substrates and acid-treated with 1 M sulfuric acid to produce PEDOT:PSS/ $\text{TiO}_2$  mixed thin films. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy and ultraviolet-visible spectroscopy (UV-vis) were used for structural characterization. TE properties were evaluated by measuring  $S$  and  $\sigma$  using a homemade device and the van der Pauw method respectively, and 365 nm LED light resources during light irradiation. UV light irradiation of the PEDOT:PSS/ $\text{TiO}_2$  mixed thin film improved the power factor due to a significant increase in  $S$ , although  $\sigma$  decreased. This is can be attributed that the carrier concentration was optimised by the transition of electrons from  $\text{TiO}_2$  to PEDOT:PSS and the de-doping of PEDOT due to UV light irradiation of the thin film.

**Keywords :** Thermoelectric materials; Conductive polymer; PEDOT:PSS; Titanium dioxide; UV light Irradiation

熱電材料は熱を電気に直接変換可能な材料であり、その性能はゼーベック係数  $S$  と電気伝導率  $\sigma$  を用いて出力因子 ( $S^2\sigma$ ) で評価される。有機熱電材料である PEDOT:PSS は、熱電材料に有利な低い熱伝導率  $\kappa$  と優れた柔軟性を持つ材料であるが、性能は未だ低い。酸化チタン ( $\text{TiO}_2$ ) は紫外光照射により電子を放出する特性を持つ<sup>[1]</sup>。本研究では PEDOT:PSS に  $\text{TiO}_2$  を混合し紫外光を照射することで、熱電性能を向上させることを目指した。混合溶液をガラス基板にスピコート、アニールし、1 M 硫酸で酸処理を行い PEDOT:PSS/ $\text{TiO}_2$  混合薄膜を作製した。構造評価は走査型電子顕微鏡 (SEM)、エネルギー分散型 X 線分析 (EDX)、ラマン分光法、紫外可視分光法 (UV-vis) を行った。物性測定は自作装置で  $S$ 、Van der Pauw 法で  $\sigma$  を測定し、365 nm の LED 光源を用いて光照射時の  $S$ 、 $\sigma$  測定を行った。PEDOT:PSS/ $\text{TiO}_2$  混合薄膜に紫外光を照射すると  $\sigma$  は減少したが、 $S$  が大幅に増加したため出力因子が向上した。これは紫外光照射により、 $\text{TiO}_2$  から PEDOT:PSS に電子が遷移し PEDOT の脱ドーピングが引き起こされ、キャリア濃度が最適化されたためであると考えられる。

1) GUPTA Shipra Mital *et al*, *Chin. Sci. Bull*, **2011**, 56, 16, 1639-1657



## Solid Electrolyte Interphase (SEI) の電荷貯蔵を利用した蓄電デバイスの開発

(関西大<sup>1)</sup>) ○喜田 大地<sup>1</sup>・出口 三奈子<sup>1</sup>・石川 正司<sup>1</sup>

Development of Energy Storage Devices Utilizing Charge-Storage inside Solid Electrolyte Interphase (SEI) (<sup>1</sup>*Kansai University*)○Taichi Kida,<sup>1</sup> Minako Deguchi,<sup>1</sup> Masashi Ishikawa<sup>1</sup>

To improve the energy density of lithium-ion batteries (LIBs), we propose a novel working principle using activated carbon as an anode material. When activated carbon is used as the anode material, charge/discharge tests show a high specific capacity that cannot be explained by a normal electric double layer<sup>1)</sup>. In our previous study, we reported that this charge storage mechanism is due to the formation of solid-solid interface electric double layer (SS-EDL)<sup>2)3)</sup>. The solid phase refers to the solid electrolyte interphase layer (SEI) and the electrode, and the lithium ions desolvated by SEI form an electric double layer at the interface between the electrode and SEI, which should contribute to the high capacitance.

In SS-EDL, the condition of the interface between the electrode and SEI is an important factor that determines the performance. It is also assumed that this is affected by the active material, activated carbon. In this study, we investigated the influence of the characteristics of the activated carbon on the electrochemical properties by evaluating the physical properties, electrochemical evaluation, and SEI analysis of mesopore- and micropore-based activated carbons. The results showed that the microporous activated carbon had a low charge/discharge capacity, while the mesoporous activated carbon had a high capacity. The physical property evaluation revealed that this variation depends on the formation state of SEI.

**Keywords :** *Lithium Ion Battery, Solid Electrolyte Interphase, Electric Double Layer*

リチウムイオン電池 (LIBs) のエネルギー密度向上のため、我々は、負極材料として活性炭を用いた新規な作動原理を提案する。活性炭を負極材料とした場合、充放電試験において通常の電気二重層では説明できない高い比容量を示す<sup>1)</sup>。また、当研究室の先行研究では、この電荷貯蔵機構が固相-固相界面 電気二重層 (SS-EDL)<sup>2)</sup> の形成によるものであることを報告した<sup>3)</sup>。ここで固相とは、固体電解質界面層 (SEI) と電極のことを指す。SEI により脱溶媒和されたリチウムイオンが電極と SEI の界面で電気二重層を形成することで高容量の発現に寄与していると考えられる。

SS-EDL において、電極と SEI の界面の状態は性能を左右する重要な要因である。また、これは活物質である活性炭に影響されることが推測される。本研究では、メソ孔の細孔を持つ活性炭とミクロ孔の細孔を持つ活性炭の物性評価、電気化学評価、SEI の分析を行うことで、活性炭の特徴が電気化学特性へ与える影響について調査した。

実際に、ミクロ孔活性炭では充放電容量が小さく、メソ孔活性炭では高容量という結果が得られた。また、この原因は SEI の形成形態によるものであることが物性評価から明らかとなった。

1) 大林祐介 他, 第 11 回 JACI/GSC シンポジウム, B-16 (2023)

2) Y. Z. Wang et al., *Advanced Energy Materials.*, **9**, 1803715 (2019)

3) 喜田大地 他, 第 65 回電池討論会, 1C05 (2024)

## Li 金属電極の使用に向けた LATP 系酸化物固体電解質の表面処理及び複合固体電解質への適応

(関西大<sup>1</sup>・NIMS<sup>2</sup>) ○澤田 昂明<sup>1</sup>・長谷川 源<sup>2</sup>・桑田 直明<sup>2</sup>・石川正司<sup>1</sup>

Surface Treatment of LATP-based Solid Oxide Electrolyte for Use with Li-metal Electrode and its Application to Composite Solid Electrolyte (<sup>1</sup>Kansai University, <sup>2</sup>National Institute for Materials Science) ○Komei Sawada,<sup>1</sup> Gen Hasegawa,<sup>2</sup> Naoaki Kuwata,<sup>2</sup> Masashi Ishikawa<sup>1</sup>

Solid oxide electrolytes are flame retardant and have no risk of leakage compared to organic electrolytes used in conventional lithium-ion batteries (LIBs). They are therefore considered to have a very high level of safety. However, many problems remain to be solved, such as the adaptation of metal lithium (Li) electrodes for high energy density and the high energy-intensive high-temperature sintering process required for their fabrication. Therefore, our group prepared a composite solid electrolyte using a lactone-based solvent-free polymer electrolyte (1). This process should be realized with the same level of fabrication energy as that of conventional LIBs. However, the decomposition of Li due to its high reductivity could not be prevented. This is due to the reductive decomposition of the anionic framework with transition metal oxides, which is the main component of the solid oxide electrolytes. This side reaction increases the ionic conduction resistance at the electrode/electrolyte interface and causes performance degradation. Therefore, we have improved the resistance to Li reduction by molecularly coating the surface of the solid electrolyte by the hydrolysis reaction (2) of a silane coupling agent. In this presentation, we will report the fabrication method and electrochemical evaluation of the surface-treated oxide solid electrolytes.

*Keywords : Aziridine; electrochemistry; solid state ionics; interface chemistry; solid state battery; adhesion study*

酸化物固体電解質は従来のリチウムイオン電池 (LIBs) で使用される有機電解液と比較し、漏液の危険性がなく難燃性を示す。そのため非常に高い安全性を有していると考えられている。しかし、高エネルギー密度に向けた金属リチウム (Li) 電極の適応や作製するために必要となる高エネルギーを使用する高温焼結過程など解決すべき問題点が多く存在する。そこで本研究室はラクトン系無溶媒高分子電解質を用いた複合固体電解質の作製を行った<sup>1)</sup>。本開発は従来の LIBs と同程度の作製エネルギーで作製可能である。しかし、Li の高い還元性による分解を阻止することはできなかった。原因として Li による酸化物固体電解質の主成分である遷移金属酸化物を有したアニオン骨格の還元分解が挙げられる。この副反応は電極 / 電解質界面におけるイオン伝導抵抗を増加させ、性能低下を引き起こす。そこで固体電解質表面をシランカップリング剤の加水分解反応<sup>2)</sup>によってつくられた被膜で保護することで Li に対する還元耐性を向上させた。本発表では表面処理酸化物固体電解質の製造法及び電気化学評価について報告する。

### 参考文献

- 1) 澤田昂明他、電気化学会第 91 回大会要旨集、S 8-1\_3\_05 (2024)
- 2) 大橋桂他、歯科材料・器械ジャーナル、24 巻、4 号 (2005)