

アカデミックプログラム [A講演] | 19. コロイド・界面化学：口頭A講演

2025年3月26日(水) 9:30 ~ 11:40 [C]C507(第2学舎 2号館 [5階] C507)

## [[C]C507-1am] 19. コロイド・界面化学

座長：岡田 洋平、三友 秀之

## ◆ 英語

9:30 ~ 9:40

[[C]C507-1am-01]

融合反応を利用した金針状クラスターの原子精度合成

○濱崎 佑哉<sup>1</sup>、城ノ上 諒太<sup>1</sup>、高野 慎二郎<sup>1</sup>、佃 達哉<sup>1</sup> (1. 東京大学)

## ◆ 日本語

9:40 ~ 9:50

[[C]C507-1am-02]

BINAP系配位子で保護された金クラスターの合成と光特性

○リン シキ<sup>1</sup>、七分 勇勝<sup>1,2</sup>、小西 克明<sup>1,2</sup> (1. 北大院環境、2. 北大院地球環境)

## ◆ 日本語

9:50 ~ 10:00

[[C]C507-1am-03]

異種金属が導入されたサブナノ金クラスターの合成と光学特性

○許 嵐<sup>1</sup>、空翔 森田<sup>1</sup>、勇勝 七分<sup>1,2</sup>、克明 小西<sup>1,2</sup> (1. 北海道大学北大環境、2. 北大院地球環境)

## ◆ 英語

10:00 ~ 10:10

[[C]C507-1am-04]

機械学習を援用した白金族ハイレントロピー合金ナノ粒子の精密合成

○高橋 大樹<sup>1</sup>、草田 康平<sup>1,2</sup>、鳥山 誉亮<sup>3</sup>、山本 知一<sup>3</sup>、村上 恭和<sup>3,4</sup>、芦谷 拓嵩<sup>5</sup>、河口 彰吾<sup>5</sup>、坂田 修身<sup>5</sup>、北川 宏<sup>1</sup> (1. 京都大学大学院理学研究科、2. 京都大学白眉センター、3. 九州大学超顕微解析研究センター、4. 九州大学大学院工学研究院、5. JASRI/SPRing-8)

## ◆ 英語

10:10 ~ 10:20

[[C]C507-1am-05]

新規Pd-Pt-Pアモルファス合金ナノ粒子の合成と触媒特性

○池田 賢太<sup>1</sup>、向吉 恵<sup>1</sup>、草田 康平<sup>1,2</sup>、鳥山 誉亮<sup>3</sup>、山本 知一<sup>3</sup>、村上 恭和<sup>3,4</sup>、芦谷 拓嵩<sup>5</sup>、河口 彰吾<sup>5</sup>、伊奈 稔哲<sup>5</sup>、久保田 佳基<sup>6</sup>、北川 宏<sup>1</sup> (1. 京大院理、2. 京大白眉セ、3. 九大URC、4. 九大院工、5. JASRI/SPRing-8、6. 阪公大院理)

## ◆ 日本語

10:20 ~ 10:30

[[C]C507-1am-06]

9元系多元素金属硫化物ナノ粒子の合成

○金口 尚樹<sup>1</sup>、向吉 恵<sup>1</sup>、鳥山 誉亮<sup>2</sup>、山本 知一<sup>2</sup>、村上 恭和<sup>2,3</sup>、芦谷 拓嵩<sup>4</sup>、河口 彰吾<sup>4</sup>、久保田 佳基<sup>5</sup>、北川 宏<sup>1</sup> (1. 京大院理、2. 九大URC、3. 九大院工、4. JASRI/Spring-8、5. 阪公大院理)

10:30 ~ 10:40

休憩

## ◆ 日本語

10:40 ~ 10:50

[[C]C507-1am-07]

磁気粒子分光法による免疫診断のための超常磁性ナノクラスタープローブの創製に関する研究

○清水 咲弥<sup>1</sup>、酒井 歩<sup>1</sup>、高橋 麻里<sup>1</sup>、吉田 敬<sup>2</sup>、前之園 信也<sup>1</sup> (1. 北陸先端科学技術大学院大学、2. 九州大学)

◆ 日本語

10:50 ~ 11:00

[[C]C507-1am-08]

セレン化銅ナノ粒子を複合化した温度応答性高分子の合成およびその温度応答性の評価

○岡部 拓馬<sup>1</sup>、木村 美月<sup>1</sup>、坂根 駿也<sup>2</sup>、田中 秀樹<sup>1</sup> (1. 中大、2. 茨大)

◆ 日本語

11:00 ~ 11:10

[[C]C507-1am-09]

円偏光で作製したプラズモニックAu@Agナノ構造体のキラル光学効果

○高橋 輝<sup>1</sup>、石田 拓也<sup>1</sup>、立間 徹<sup>1</sup> (1. 東大生研)

◆ 日本語

11:10 ~ 11:20

[[C]C507-1am-10]

インジウムドーパ酸化亜鉛ナノ結晶の光物理・光化学特性

○永井 奏斗<sup>1</sup>、永井 邑樹<sup>1</sup>、小林 洋一<sup>1,2</sup> (1. 立命館大学、2. JST さきがけ)

◆ 日本語

11:20 ~ 11:30

[[C]C507-1am-11]

長鎖アミンを用いた金-銀ナノワイヤーの相間移動と抽出分離

○斉藤 慎治<sup>1</sup>、伊村 芳朗<sup>1</sup> (1. 東京理科大学)

◆ 日本語

11:30 ~ 11:40

[[C]C507-1am-12]

Ni水酸化物塩ナノ粒子の分散性と形態制御に向けた液相合成条件の検討

○辻本 敬一郎<sup>1</sup>、樽谷 直紀<sup>1</sup>、片桐 清文<sup>1</sup>、犬丸 啓<sup>1</sup> (1. 広島大学)

## Atomically Precise Synthesis of Gold Needle Clusters by Fusion Reactions

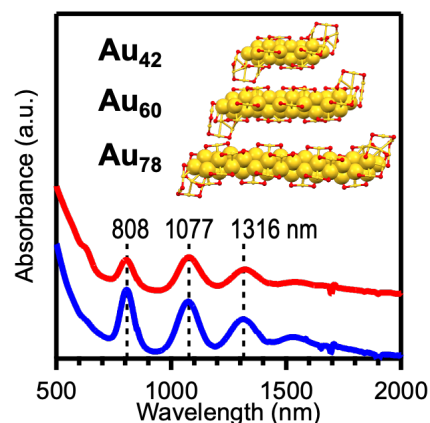
(<sup>1</sup>Department of Chemistry, School of Science, The University of Tokyo) ○ Yuya Hamasaki,<sup>1</sup> Ryota Jonoue,<sup>1</sup> Shinjiro Takano,<sup>1</sup> Tatsuya Tsukuda<sup>1</sup>

**Keywords:** Ligand-protected Metal Clusters; Anisotropic Clusters; Fusion Reaction; IR Region Absorption

Prolate gold clusters are known to exhibit intense photo-absorption bands in the NIR to IR region that redshift with aspect ratio, and are expected to find applications in fields such as bioimaging and photothermal conversion.<sup>1</sup> However, anisotropic clusters are typically thermodynamically unstable and difficult to synthesize using conventional reduction methods of Au(I) species. A plausible approach to synthesize anisotropic Au nanostructures is to fuse pre-synthesized isotropic Au clusters. We have recently reported the synthesis of bi-icosahedral MM'Au<sub>21</sub>-core (M, M' = Au, Pt, Pd) clusters via hydride-mediated fusion processes.<sup>2</sup> In this study, we found the formation of needle-like Au clusters via thermally induced sequential fusion of thiolate-protected Au clusters.<sup>3</sup>

Maran reported that incubation of a highly concentrated toluene solution of [Au<sub>25</sub>(PET)<sub>18</sub>]<sup>0</sup> (**Au<sub>25</sub>**, PET = 2-phenylethanethiolate), with an icosahedral Au<sub>13</sub> core, yields [Au<sub>38</sub>(PET)<sub>24</sub>]<sup>0</sup> (**Au<sub>38</sub>**), with a bi-icosahedral Au<sub>23</sub> core.<sup>3</sup> In contrast, the absorption spectra of the crude product heated in 1,2-dichloroethane (DCE) show, in addition to the characteristic features of **Au<sub>38</sub>**, three prominent peaks in the NIR region (red trace in Fig. 1). From the crude products, three fractions responsible for the absorptions at 808, 1077, and 1316 nm were isolated and assigned by mass spectrometry to [Au<sub>42</sub>(PET)<sub>32</sub>]<sup>0</sup> (**Au<sub>42</sub>**), [Au<sub>60</sub>(PET)<sub>44</sub>]<sup>0</sup> (**Au<sub>60</sub>**), and [Au<sub>78</sub>(PET)<sub>56</sub>]<sup>0</sup> (**Au<sub>78</sub>**), respectively. The compositions and optical properties of **Au<sub>42</sub>**, **Au<sub>60</sub>**, and **Au<sub>78</sub>** are consistent with those having the core of an Au<sub>1</sub>-(Au<sub>3</sub>)<sub>2n</sub>-Au<sub>1</sub> structure with *n* = 3, 5, and 7, respectively.<sup>1</sup> Similar optical spectra were observed by heating a highly concentrated solution of [Au<sub>24</sub>(PET)<sub>20</sub>]<sup>0</sup> (**Au<sub>24</sub>**) with the Au<sub>1</sub>-(Au<sub>3</sub>)<sub>2</sub>-Au<sub>1</sub> core<sup>4</sup> (blue trace in Fig. 1). These observations suggest that the **Au<sub>24</sub>** is involved as a key intermediate in the fusion reaction, illustrating the effectiveness of cluster fusion reactions in synthesizing needle clusters.

1) L. Luo *et al.* *PNAS* **2024**, *121*, e2318537121. 2) E. Ito *et al.* *Angew. Chem. Int. Ed.* **2021**, *60*, 645. 3) T. Dainese *et al.* *ACS Nano* **2018**, *12*, 7057. 4) Z. Gan *et al.* *Angew. Chem. Int. Ed.* **2016**, *55*, 11567.



**Fig. 1.** Absorption spectra of crude after heating (red) **Au<sub>25</sub>** and (blue) **Au<sub>24</sub>** in DCE. Inset: structure of product clusters (Au: yellow, S: red. C, H: omitted for clarity)<sup>1</sup>.

## BINAP 系配位子で保護された金クラスターの合成と光特性

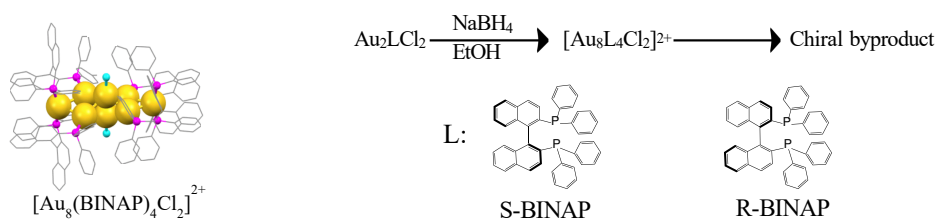
(北大院環境<sup>1</sup>・北大地球環境<sup>2</sup>) ○林 士琦<sup>1</sup>・七分 勇勝<sup>1,2</sup>・小西 克明<sup>1,2</sup>

Synthesis and optical properties of gold clusters protected by BINAP-type ligands (<sup>1</sup>*Grad. School of Env. Sci., Hokkaido Univ.*, <sup>2</sup>*Fac. of Env. Earth Sci., Hokkaido Univ.*) ○Shiqi Lin<sup>1</sup>, Yukatsu Shichibu<sup>1,2</sup>, Katsuaki Konishi<sup>1,2</sup>

The synthesis of gold clusters protected by multidentate ligands has recently attracted attention. In our lab, we have synthesized various gold clusters and explored their unique structures and functions. For instance, using chiral ligands, we successfully created gold clusters with distinct core structures, such as Au<sub>24</sub> with a double-helical Au<sub>12</sub> and Au<sub>13</sub> with a distorted pentagonal bipyramidal Au<sub>10</sub>. These results showed that even small ligand changes can lead to completely different gold core structures. In this study, we synthesized Au<sub>8</sub> clusters ligated with chiral BINAP ligands from the reduction of a Au<sub>2</sub> complex. We also discovered a chiral byproduct and explored how changes in its ligand shell affect the optical properties.

**Keywords :** Gold cluster; Chiral

多座配位子で保護された金クラスターの合成は近年注目を集めている。当研究室では様々なジホスフィン配位金クラスターの合成を行い、ユニークな構造・機能を明らかにしてきた。例えば、キラルなジホスフィン配位子を用いると二重らせん Au<sub>12</sub>を含む Au<sub>24</sub> コア<sup>1)</sup>や反五角柱 Au<sub>10</sub>を含む Au<sub>13</sub> コア<sup>2)</sup>をもつ金クラスターの合成に成功しており、わずかな配位子構造の違いから全く異なる金コア構造が形成されることがわかった。本研究では、キラルなジホスフィンである BINAP 系配位を用い、Au<sub>2</sub> 錯体を還元することから Au<sub>8</sub> クラスターの合成（下図）に成功し、類似のクラスターとの比較により、配位子シェル環境がクラスターの幾何構造や光学特性に与える影響を明らかにした。また、核数の異なる副生成物を発見し、その特性を調べた。



1) M Sugiuchi, Y Shichibu, K Konishi, *Angew. Chem., Int. Ed. (Communication)*, **2018**, 57, 7855.

2) Y Shichibu, K Konishi, *Small*, **2010**, 6, 1216.

## 異種金属が導入されたサブナノ金クラスターの合成と光学特性

(北大院環境<sup>1</sup>・北大地球環境<sup>2</sup>) ○許嵐<sup>1</sup>・森田 空翔<sup>1</sup>・七分 勇勝<sup>1,2</sup>・小西克明<sup>1,2</sup>  
 Synthesis and Optical Properties of Sub-Nano Gold Clusters Incorporating Heterometals.  
 (<sup>1</sup>Graduate School of Environment Science, Hokkaido University, <sup>2</sup>Graduate School of  
 Environment Science, Hokkaido University) ○Lan Xu,<sup>1</sup>Hiroto Morita,<sup>1</sup> Yukatsu Shichibu,<sup>1,2</sup>  
 Katsuaki Konishi<sup>1,2</sup>

Diphosphine-protected subnano gold clusters have different optical properties depending on their nuclearities and geometries<sup>1)</sup>. We have found that a Au<sub>6</sub> cluster protected by 2,6-bis(diphenylphosphino)pyridine (2,6-PyDP) transformed into a Au<sub>7</sub> cluster via spontaneous cluster growth under room light. In this study, we synthesized alloy clusters by heterometals M (M = Cu, Ag) with the Au<sub>6</sub> cluster. Formation of alloy clusters were confirmed from ESI-MS spectra. X-ray analysis revealed that the alloy clusters adopt an Au<sub>6</sub>M<sub>2</sub> cluster structure, where the metal complexes cap the Au<sub>6</sub> cluster. Photoluminescence measurements revealed the efficient emission for Au<sub>6</sub>Cu<sub>2</sub>, the quantum yield of which was about 30 %. We are also attempting to synthesize alloy clusters with other metals.

**Keywords:** Gold cluster, Alloy, Colloid

ジホスフィン配位子で保護されたサブナノ金クラスターは、核数や構造に依存した特異な光学特性を示す<sup>1)</sup>。これまで当研究室では、ピリジン修飾ジホスフィン配位子 (2,6-PyDP) で保護された Au<sub>6</sub> クラスターが室内光下で自発的な核成長を経て Au<sub>7</sub> クラスターへ変化することが分かった。本研究では、Au<sub>6</sub> クラスターに異種金属 M (M = Cu, Ag) を共存させることで合金クラスターの合成を試みた。合成物の ESI-MS スペクトルにより Au<sub>6</sub>M<sub>2</sub> クラスターの形成を確認した。単結晶 X 線構造解析の結果、Au<sub>6</sub> クラスターに金属錯体がキャップされた Au<sub>6</sub>M<sub>2</sub> クラスター構造が明らかとなった (Figure 1a)。さらに、PL 測定では、Au<sub>6</sub>Cu<sub>2</sub> で 29.9 %、Au<sub>6</sub>Ag<sub>2</sub> で 4 %の量子収率示し、Cu のほうが約 8 倍高かった (Figure 1 b)。本発表では、他の金属を用いた合金クラスターの合成の試みについても報告する。

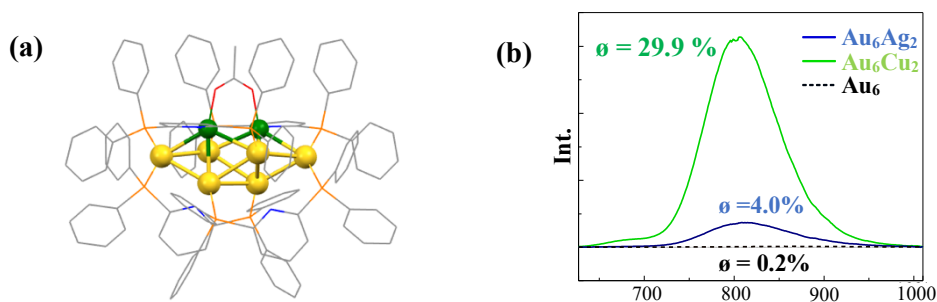


Figure 1 クラスターの (a) 幾何構造 (M = Cu) と (b) 発光スペクトル

- 1) K. Konishi, M. Iwasaki, Y. Shichibu, *Acc. Chem. Res.* **2018**, *51*, 3125-3133.

## Precise Flow Synthesis of Platinum-Group-Metal High-Entropy Alloy Nanoparticles by Machine Learning

(<sup>1</sup>Grad. Sch. Sci., Kyoto Univ., <sup>2</sup>Hakubi Center, Kyoto Univ., <sup>3</sup>URC, Kyushu Univ., <sup>4</sup>Grad. Sch. Eng., Kyushu Univ., <sup>5</sup>JASRI/SPring-8) ○Daiki Takahashi,<sup>1</sup> Kohei Kusada,<sup>1,2</sup> Takaaki Toriyama,<sup>3</sup> Tomokazu Yamamoto<sup>3</sup>, Yasukazu Murakami<sup>3,4</sup>, Hirotaka Ashitani<sup>5</sup>, Shogo Kawaguchi<sup>5</sup>, Osami Sakata<sup>5</sup>, Hiroshi Kitagawa<sup>1</sup>

**Keywords:** High-Entropy Alloy, Nanoparticles, Machine Learning

High-entropy alloy nanoparticles (HEA NPs) are solid-solution alloys with particle size in the nanometer scale, composed of five or more metals at almost equimolar compositions. Their high catalytic activities cannot be explained by a simple combination of constituent elements<sup>1)</sup>, and the origin of these unique properties has been still discussed. In addition, precisely synthesizing HEA NPs is challenging because each element has different characteristics such as redox potential and atomic radius, which hinders the further elucidation of their catalytic mechanisms. Here, we report the synthesis of IrPdPtRhRu HEA NPs with small and homogeneous particle sizes through flow synthesis which can realize a continuous and uniform reaction environment<sup>2)</sup>. This method involves various synthesis parameters influencing crystal growth and alloy formation, and a comprehensive understanding of each parameter's contribution leads to the precise synthesis of HEA NPs.

As a result, the smallest-size HEA NPs obtained by flow synthesis was  $2.4 \pm 0.5$  nm. The samples were characterized by scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDS) (Fig.1), and powder X-ray diffraction. To evaluate the contribution of each synthesis parameter, machine learning with partial least squares method was performed. A simple model of linear combination with the synthesis parameters gave a good predictive performance, and it showed that the particle size decreased with the increasing flow rate of the reductant solution. Furthermore, we discuss whether machine learning can tell suitable synthetic conditions to provide homogeneously alloyed HEA NPs.

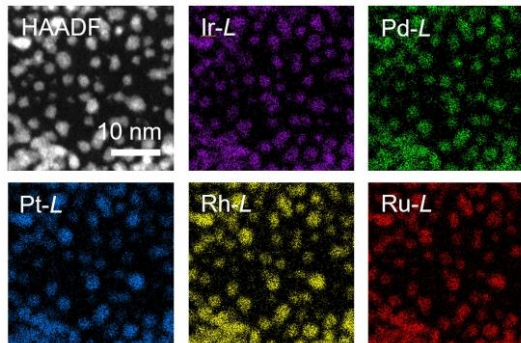


Fig.2 HAADF-STEM image of IrPdPtRhRu HEA NPs and EDS maps of constituent elements

- 1) D. Wu *et al.*, *J. Am. Chem. Soc.*, **144**, 3365–3369 (2022).
- 2) K. Kusada *et al.*, *J. Phys. Chem. C*, **125**, 1, 458–463 (2021).

## Synthesis of novel Pd–Pt–P amorphous nanoparticles and catalytic activity

(<sup>1</sup>Graduate School of Science, Kyoto University, <sup>2</sup>Hakubi Center, Kyoto University, <sup>3</sup>URC, Kyushu University, <sup>4</sup>Graduate School of Engineering, Kyushu University, <sup>5</sup>JASRI/SPRING-8, <sup>6</sup>Graduate School of Science, Osaka Metropolitan University.) ○ Kenta Ikeda,<sup>1</sup> Megumi Mukoyoshi,<sup>1</sup> Kohei Kusada,<sup>1,2</sup> Takaaki Toriyama,<sup>3</sup> Tomokazu Yamamoto,<sup>3</sup> Yasukazu Murakami,<sup>3,4</sup> Hirotaka Ashitani,<sup>5</sup> Shogo Kawaguchi,<sup>5</sup> Toshiaki Ina,<sup>5</sup> Yoshiki Kubota,<sup>6</sup> Hiroshi Kitagawa<sup>1</sup>

**Keywords:** Amorphous; Nanoparticles; Electrochemical catalysts

Atomic arrangement is one of the dominant factors to control materials' property.<sup>1</sup> Especially, amorphous materials have attracted much attention because of their complex structure and high performance as a solid catalyst derived from many dangling bonds.<sup>2</sup> For Pt nanoparticles showing high activity for electrochemical reactions such as hydrogen evolution reaction (HER), however, there have been a few reports on the control of its atomic arrangements. This is due to the high stability of fcc crystalline structure and low stability of amorphous state for Pt.

We succeeded to synthesize Pt-containing amorphous nanoparticles (ANPs) by alloying Pt with PdP ANPs.<sup>3</sup> All the syntheses were conducted by a wet chemical reduction method in oleylamine system. The amorphous structure was characterized by XRD (Figure 1) and atomic resolution HAADF-STEM image. By STEM-EDX and STEM-EELS (Figure 2), it was confirmed that Pd, Pt and P are homogeneously distributed in the particle. The catalytic activity for HER was investigated by a three-electrode electrochemical measurement and compared with the same composition crystalline nanoparticles.

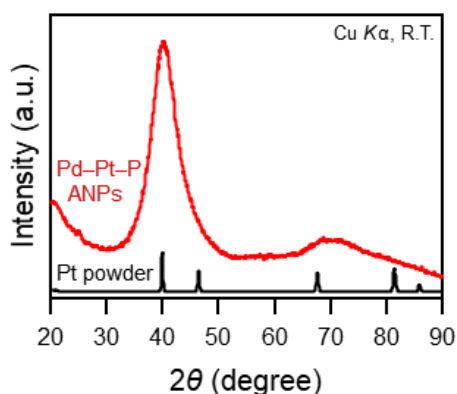


Figure 1. PXRD profile of Pd–Pt–P ANPs

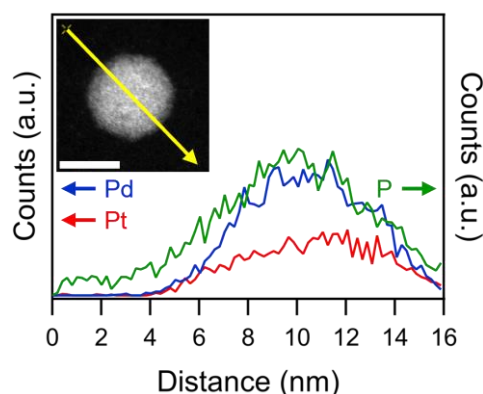


Figure 2. EDX line scan profiles of Pd (blue) and Pt (red) and EELS line scan profiles of P (green) of the ANP. The arrow shows the region of interest. Scale bar is 5 nm.

1) Q. Zhang et al. *Nat. Commun.* **2018**, 9, 510, 2) S. Anantharaj et al. *Small* **2020**, 16, 1905779, 3) K. Ikeda et al. *Chem. Lett.* **2024**, 53, 144.



## 前期遷移金属からなる多元系金属硫化物ナノ粒子の合成

(京大院理<sup>1</sup>・九大 URC<sup>2</sup>・九大院工<sup>3</sup>・JASRI/Spring-8<sup>4</sup>・阪公大院理<sup>5</sup>) ○金口 尚樹<sup>1</sup>、向吉 恵<sup>1</sup>、鳥山 誉亮<sup>2</sup>、山本 知一<sup>2</sup>、村上 恭和<sup>2,3</sup>、芦谷 拓嵩<sup>4</sup>、河口 彰吾<sup>4</sup>、久保田 佳基<sup>5</sup>、北川 宏<sup>1</sup>

Synthesis of Multi-Element Metal Sulfide Nanosheets Composed of Early Transition Metal (<sup>1</sup>Grad. Sch. Sci., Kyoto Univ., <sup>2</sup>URC, Kyushu Univ., <sup>3</sup>Grad. Sch. Eng., Kyushu Univ., <sup>4</sup>JASRI/Spring-8, <sup>5</sup>Grad. Sch. Sci., Osaka Metro. Univ.) ○Naoki Kaneguchi<sup>1</sup>, Megumi Mukoyoshi<sup>1</sup>, Takaaki Toriyama<sup>2</sup>, Tomokazu Yamamoto<sup>2</sup>, Yasukazu Murakami<sup>2,3</sup>, Hiroataka Ashitani<sup>4</sup>, Shougo Kawaguchi<sup>4</sup>, Yoshiki Kubota<sup>5</sup>, Hiroshi Kitagawa<sup>1</sup>

Transition-metal sulfides have a high surface area and tunable band gap derived from their layered structure. Their unique physical properties have led to their application in various fields such as catalysts, transistors, and photovoltaics. In recent years, there have been many studies on unary metal sulfides, but there are still few reports on the synthesis of multi-element sulfides especially composed of early transition metals. In this study, we report the synthesis of multi-element sulfides composed of early transition metals by a wet chemical method, in which metal ions react with carbon disulfide or sulfur in oleylamine solution. The results of structural characterization suggest that the obtained nanoparticles are multi-element metal sulfides with a MoS<sub>2</sub>-like layered structure.

**Keywords :** Multi-Element nanoparticles, Metal sulfide, Nanosheet

遷移金属硫化物は層状構造由来の高表面積や調節可能なバンドギャップを持つ。その特異な物性により、触媒、トランジスタ、太陽光発電などの様々な分野で応用が期待されている。現在、遷移金属硫化物の研究は一元系が主であり、前期遷移金属の多元系硫化物の合成の報告はまだ少ない。本研究では、オレイルアミン溶液中で金属イオンと二硫化炭素または硫黄を反応させる溶液法により、前期遷移金属の多元系金属硫化物の合成を行った。

構造同定の結果から、得られたナノ粒子は数種類の金属が固溶した MoS<sub>2</sub> 状の層状構造を持つ多元系金属硫化物だと示唆され、原子層数層からなるナノシートの集合体であることが分かった。

図 生成物の粉末 X 線回折パターン

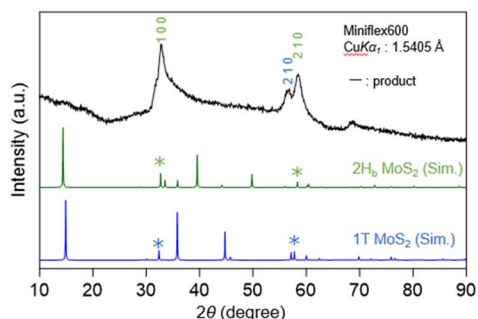


表 蛍光 X 線分析結果

Metal	mol %
Ti	5.17
Zr	2.55
Hf	3.40
V	7.66
Nb	4.87
Ta	3.50
Mo	5.83
W	6.84
S	60.17



## Study on the Development of Superparamagnetic Nanocluster Probes for Immunodiagnostics using Magnetic Particle Spectroscopy

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**Keywords:** Superparamagnetism; Nanoparticle; Magnetic nanocluster; Magnetic particle spectroscopy; Multi-antigen detection

Magnetic particle spectroscopy (MPS)<sup>1)</sup> which provides relatively rapid and accurate detection of antigens. In addition, it is possible to perform multiple antigen detection based on the principle of MPS. The basic principle of MPS is to obtain information about the environment near superparamagnetic nanoparticles (SPMNPs) by analyzing the higher frequency of the magnetic response of SPMNPs in an external alternating magnetic field (AMF). In immunodiagnosis by MPS subtle changes in Brownian relaxation due to antigen binding are detected as changes in odd harmonic intensity. The presence or absence of the antigen is determined by detecting the subtle changes in Brownian relaxation caused by antigen binding as changes in the intensity of odd harmonics. Magnetic nanoclusters (MNCs) are suitable as MPS probes because Brownian relaxation is dominant in nanoclusters due to magnetic coupling between primary particles. In this study,  $M\text{Fe}_2\text{O}_4$  ( $M = \text{Fe}, \text{Co}, \text{Zn}$ ) MNCs with different magnetic properties were prepared for the creation of MNC probes for MPS.

$M\text{Fe}_2\text{O}_4$  MNC was synthesised by a solvothermal method. For example, Fig. 1a shows a TEM image of  $\text{CoFe}_2\text{O}_4$  (CFO) MNCs, which were found to be aggregates of CFO SPMNPs. The primary particle size was  $8.4 \pm 1.7$  nm and cluster size was  $61.1 \pm 8.1$  nm. Avidin, used as an antigen model, was adsorbed onto the surface of these CFO MNCs by electrostatic interaction and alternating current susceptibility (ACS) and MPS measurements were performed. The ACS measurements showed that Brownian relaxation was suppressed by the adsorption of avidin (Fig. 1b), while the MPS measurements showed that the suppression of Brownian relaxation caused a difference in the intensity of the higher harmonics (Fig. 1c). In this study, we will present results of different MNCs with different magnetic properties.

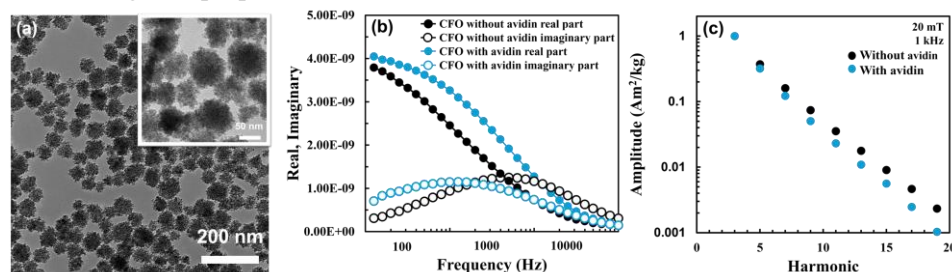


Fig.1 (a) TEM image of CFO MNCs. (Inset: High magnification image of CFO MNCs). (b) ACS measurement results. (c) MPS measurement results.

1) K. Wu *et al*, *ACS Appl. Mater. Interfaces*, **2021**, *13*, 44136.

セレン化銅ナノ粒子を複合化した温度応答性高分子の合成および  
その温度応答性の評価 (中央院理工<sup>1</sup>・中央理工<sup>2</sup>・茨大院理工  
<sup>3</sup>) ○岡部拓馬<sup>1</sup>、木村美月<sup>2</sup>、坂根駿也<sup>3</sup>、田中秀樹<sup>1,2</sup>)

Synthesis of Temperature-Responsive Polymers Combined with Copper Selenide Nanoparticles and Evaluation of Their Thermal Responsiveness (<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*) ○Takuma Okabe<sup>1</sup>, Mizuki Kimura<sup>2</sup>, Shunya Sakane<sup>3</sup>, Hideki Tanaka<sup>1,2</sup>

Semiconductor nanoparticles exhibit localized surface plasmon resonance (LSPR) absorption when surface free carriers undergo collective oscillation upon light irradiation. This leads to localized heating near the nanoparticles. Specifically, by combining nanoparticles with the thermoresponsive polymer PNIPAM (poly(*N*-isopropylacrylamide)), the nanoparticles can function as photothermal agents, enabling temperature elevation and phase separation of PNIPAM upon light irradiation. Since PNIPAM exhibits a lower critical solution temperature (LCST) near body temperature, it holds promise for applications in drug delivery systems (DDS). However, for DDS applications, it is essential to convert biologically penetrable and non-invasive near-infrared (NIR) light into heat. In this study, composite materials of copper selenide nanoparticles and PNIPAM were synthesized to achieve plasmon absorption in the NIR region. The precursor molar ratio of Cu and Se was varied during the synthesis. Structural evaluations were performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), UV-vis-NIR spectroscopy, and dynamic light scattering (DLS).

Regardless of the Cu-to-Se precursor ratio, cubic Cu<sub>2-x</sub>Se was formed. When the Cu:Se ratio was 1:1, LSPR absorption appeared around 1100 nm. In contrast, at a Cu:Se ratio of 2:1, an absorption peak near 1400 nm intensified over time and blue-shifted to around 1100 nm.

**Keywords** : Plasmonic heating, Copper selenide, Nanoparticles, Thermoresponsive polymer

半導体ナノ粒子は光照射によって表面の自由キャリアが集団振動することで局在表面プラズモン吸収 (LSPR) が生じる。これにより粒子近傍が局所的に加熱される。特に、温度応答性高分子である PNIPAM (ポリ(*N*-イソプロピルアクリルアミド)) とナノ粒子を複合化することでナノ粒子は光熱剤として機能し、光照射に伴う温度上昇と PNIPAM の相分離が可能となる。PNIPAM は体温近傍に LCST (下限臨界溶液温度) をもつため、ドラッグデリバリーシステム (DDS) への応用が期待されている。しかし、DDS への応用には細胞非侵襲で生体透過性の高い近赤外光を熱に変換する必要がある。そのため、本研究では近赤外領域のプラズモン吸収を目指し、セレン化銅ナノ粒子と PNIPAM の複合材料を合成することを目的とした。室温での合成が可能な化学還元法により Cu と Se の前駆体の仕込み比を変化させたセレン化銅ナノ粒子と PNIPAM の複合材料を合成した。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)、紫外可視近赤外分光法 (UV-vis-NIR)、動的光散乱 (DLS) を行った。

Cu と Se の仕込み比によらず、立方晶の Cu<sub>2-x</sub>Se が生成した。Cu : Se = 1 : 1 のときは 1100 nm 付近に LSPR 吸収が生じた一方で、Cu : Se = 2 : 1 のときは 1400 nm 付近の吸収ピークが時間経過に伴い強度が増大し、1100 nm 付近までブルーシフトした。

## 円偏光で作製したプラズモニック Au@Ag ナノ構造体のキラル光学効果

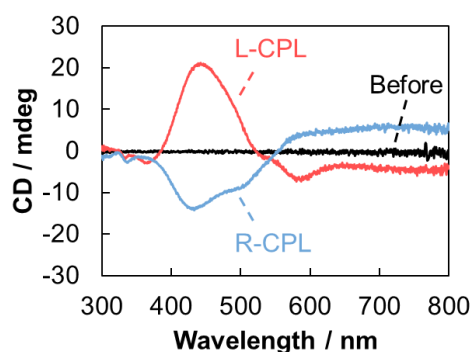
(東大生研) ○高橋 輝・石田 拓也・立間 徹

Chiroptical Effects of Plasmonic Au@Ag Nanostructures Fabricated by Circularly Polarized Light (IIS, The Univ. of Tokyo) ○Hikaru Takahashi, Takuya Ishida, Tetsu Tatsuma

Plasmonic nanoparticles with chiral shapes exhibit strong chiroptical responses, and should be suitable for application in chiral molecule sensors and metamaterials. We have developed simple and convenient methods for chiral shaping of nanoparticles by utilizing circularly polarized light (CPL) as the chiral source. Hot holes or electrons generated by CPL are used for oxidative<sup>1-4)</sup> or reductive<sup>5)</sup> deposition, respectively, for the chiral shaping. In the case of reductive deposition, it has been difficult to fabricate clearly chiral structures, and it is important to achieve precise shape control. In the present study, we fabricated chiral Au@Ag nanostructures by combining hot electron generation according to chiral electric distribution<sup>6)</sup> around achiral Au nanocubes under CPL, with preferential deposition of Ag on Au{111} and {110} planes. The Au@Ag nanostructures thus obtained exhibited circular dichroism in the wavelength regions corresponding to their plasmon resonance (Fig. 1). Furthermore, we performed electromagnetic field analysis using an FDTD method to investigate the chiral shaping process and their resultant optical responses.

**Keywords :** Chiroptical Effect, Metal Nanoparticle, Circularly Polarized Light, Localized Surface Plasmon Resonance, Nanofabrication

キラルな形状を持つプラズモニックナノ構造は、強いキラル光学応答を示し、キラル分子センサやメタマテリアルへの応用が期待される。我々は、円偏光をキラル源としたキラルナノ構造体の簡便な作製法を開発しており、熱正孔による酸化析出<sup>1-4)</sup>や、熱電子による還元析出<sup>5)</sup>を利用したキラルナノ構造体作製を行ってきた。還元析出では、全てプラズモニックな金属からなる構造を作れるメリットはあるが、明瞭なキラル形状を得ることが難しく、精密な形状制御が課題である。本研究では、アキラルな Au ナノキューブに円偏光を照射し、それにより生じるキラルな電場分布<sup>6)</sup>に従った熱電子生成と、AuNC の{111}面と{110}面における Ag の優先的還元析出により、キラル Au@Ag ナノ構造体を作製した。このナノ構造体はプラズモン共鳴波長域で円偏光二色性を示した (Fig. 1)。また、FDTD 電磁場解析法により、ナノ構造体のキラル形状化過程や光学応答を解析した。



**Figure 1.** CD spectra before or after CPL irradiation.

1) K. Saito and T. Tatsuma, *Nano Lett.* **2018**, *18*, 3209. 2) K. Morisawa, T. Ishida, and T. Tatsuma, *ACS Nano* **2020**, *14*, 3603. 3) K. Shimomura, Y. Nakane, T. Ishida, and T. Tatsuma, *Appl. Phys. Lett.* **2023**, *122*, 151109. 4) T. Homma, N. Sawada, T. Ishida, and T. Tatsuma, *ChemNanoMat* **2023**, *9*, e202300096. 5) T. Ishida, A. Isawa, S. Kuroki, Y. Kameoka, and T. Tatsuma, *Appl. Phys. Lett.* **2023**, *123*, 061111. 6) N. Ichiji, T. Ishida, I. Morichika, T. Tatsuma, and S. Ashihara, *Phys. Rev. B* **2024**, *109*, 035428.

## インジウムドーピング酸化亜鉛ナノ結晶の光物理・光化学特性

(立命館大生命科学<sup>1</sup>・JST さきがけ<sup>2</sup>) ○永井 奏斗<sup>1</sup>・永井 邑樹<sup>1</sup>・小林 洋一<sup>1,2</sup>  
 Photophysical and photochemical properties of indium-doped zinc oxide nanocrystals  
 (<sup>1</sup>Ritsumeikan Univ.,<sup>2</sup>PRESTO JST) ○Kanato Nagai,<sup>1</sup> Yuki Nagai,<sup>1</sup> Yoichi Kobayashi<sup>1,2</sup>

A degenerate semiconductor is a semiconductor in which the doping level is so high that the Fermi level moves into the conduction or valence bands, leading to metallic-like behavior. Nanocrystals (NCs) of degenerate semiconductors have unique optical properties such as size-dependent localized surface plasmon resonance and have attracted attention recently. Among various degenerate semiconductors, indium-doped zinc oxide nanocrystals (IZO NCs) have attracted significant attention due to their cost-effectiveness and lower toxicity compared to indium tin oxide.<sup>1</sup> However, their photophysical processes and even photochemical processes remain elusive. In this study, we synthesized IZO NCs with different indium doping rates and examined their optical properties.

**Keywords :** Indium doped zinc oxide; Degenerate semiconductor; Semiconductor nanocrystals; Auger recombination; Plasmon resonances

高濃度ドーピングによってフェルミ準位が伝導帯内に存在する縮退半導体のナノ結晶(NCs)は、局在表面プラズモン共鳴などの特異的な光学特性を有している。その中でも、インジウムをドーピングした酸化亜鉛(IZO) NCs は低コストで毒性が低いことから、近年注目されている。しかし、光励起によるキャリアダイナミクスや化学反応の詳細は十分に解明されていない。本研究では、インジウムの添加率の異なる IZO NCs を合成し、その光学特性を調べたので報告する。

ZnO NCs のバンド間遷移の吸収端は 372 nm である一方、インジウムドーピングに伴い短波長側(358 nm)にシフトした(Fig. 1a)。また、近赤外領域で伝導電子に起因する広帯域なプラズモン共鳴吸収が確認された。

347 nm の励起光を用いた際の IZO NCs (粒径 = 11.4 nm、In/Zn = 6.3 mol%) の過渡吸収スペクトルを Fig. 1b に示す。400 nm の負の吸収はバンド端遷移による吸収であり、可視光領域に広がる正の吸収帯は生成されたキャリアのバンド内遷移に起因する。励起状態ダイナミクスの詳細については、当日に発表する。

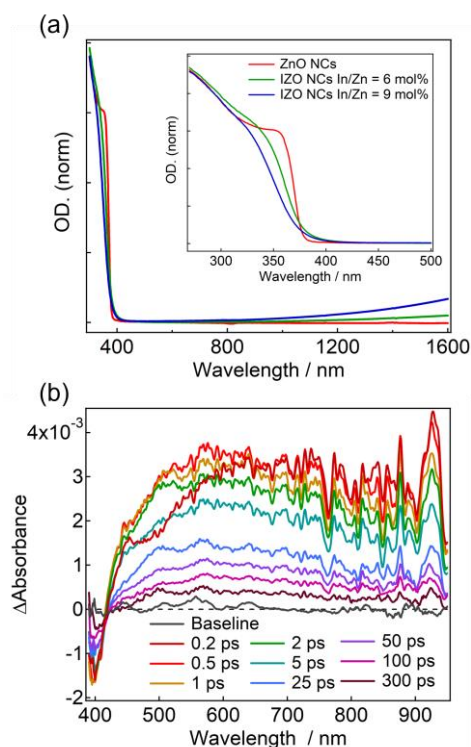


Fig. 1 (a) Absorption spectra of ZnO NCs with different indium doping ratios. (b) Transient absorption spectra of IZO NCs(In/Zn = 6.3 mol%) in chloroform excited at 347 nm.

## 長鎖アミンを用いた金－銀ナノワイヤーの相間移動と抽出分離

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Phase transfer and fractionation of gold and silver bimetallic nanowires using long-chain amine  
(Tokyo University of Science) ○Shinji Saito, Yoshiro Imura

Noble metal nanowires are attractive because of their unique optical and catalytic properties. Previously, we reported the preparation and fractionation of Au nanowires and spherical Au nanoparticles using long-chain amine (C18AA) as a capping agent. In addition, Au-Ag nanowires were synthesized using C18AA as a capping agent, while spherical nanoparticles were also obtained. It is expected that the original properties of the Au-Ag nanowires appeared by fractionation of Au-Ag nanowires and spherical nanoparticles. In this study, we conducted fractionation of Au-Ag nanowires and spherical nanoparticles by phase transfer method using C18AA. The phase transfer method was performed by adding water to the Au-Ag nanowire in toluene. As a result, it was found that Au-Ag nanowires were extracted to the water phase from Au nanocrystals in toluene.

**Keywords :** Nanowire; Nanocrystal; Phase transfer; Fractionation

貴金属ナノワイヤーは、特異的な光学特性および触媒特性を示すため注目を集めている。これまでに、長鎖アミン(C18AA)を保護剤に用いることで金ナノワイヤーが合成され、相間移動操作を行うことで副生成物である球状金ナノ粒子と分離できることを報告した。さらに、C18AA を保護剤に用いることで、金－銀ナノワイヤーが形成されることも明らかにした<sup>1)</sup>。金－銀ナノワイヤーを合成した際に、副生成物として球状ナノ粒子が形成するため、ナノワイヤー本来の特性を発揮するためには球状ナノ粒子と分離することが必要である。そこで、本研究では C18AA を保護剤に用いて合成した金－銀ナノワイヤーに対して相間移動操作を行い、金－銀ナノワイヤーと球状ナノ粒子の抽出分離に取り組んだ。

金－銀ナノワイヤーはC18AA水溶液に塩化金酸と硝酸銀水溶液を加えた後、アスコルビン酸を添加して合成した。その後、金－銀ナノワイヤー分散液の溶媒を除去し、トルエンを加えることで、トルエンに分散した金－銀ナノワイヤーを得た。この分散液に水を加え、数日間静置した後に、水相とトルエン相を紫外可視吸収スペクトル測定により評価した。その結果、相間移動前はナノワイヤーによる赤外領域の光吸収と球状ナノ粒子由来の光吸収ピークが観察されたが、相間移動後の水相では球状ナノ粒子由来のピークが見られなかった(Figure 1)。

1) Y. Imura, T. Morita, C. Morita-Imura, T. Kawai, *Colloids and Surfaces A*, **2018**, 543, 9-14.

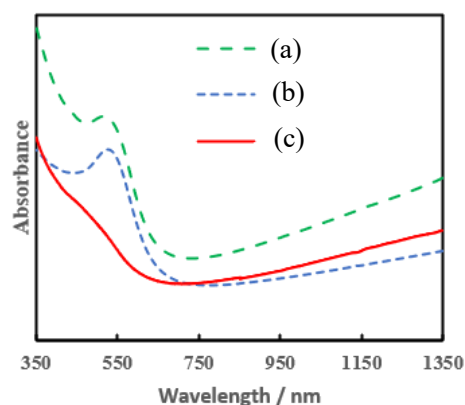


Figure 1. UV-vis spectra (a) before and (b,c) after phase transfer. (b) and (c) are toluene phase and water phase, respectively.

## Ni 水酸化物塩ナノ粒子の分散性と形態制御に向けた液相合成条件の検討

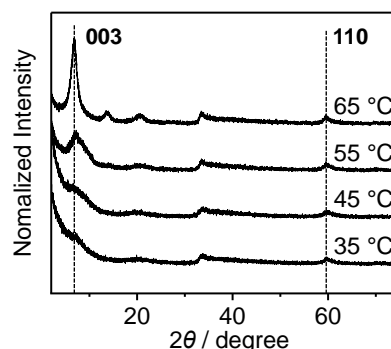
(広島大院先進理工) ○辻本 敬一郎・樽谷 直紀・片桐 清文・犬丸 啓

Investigation of Liquid-Phase Synthesis Conditions toward Control of Dispersibility and Morphology of Nickel Hydroxide Salt Nanoparticles (*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Keiichiro Tsujimoto, Naoki Tarutani, Kiyofumi Katagiri, Kei Inumaru

In the liquid-phase synthesis of nanoparticles, surface modification with bulky molecules and/or polymers is crucial to prevent aggregation and excessive crystal growth due to physical contact. In contrast, we have found that metal hydroxide salt nanoparticles can form and stably disperse even under highly concentrated conditions by using small molecules such as 2-propenoic acid. In this study, we investigated the effects of synthetic parameters, including reaction temperature, solvent, precursor concentration, and basic reagents, on the size, morphology and dispersibility of the resultant layered nickel hydroxide salt particles. Specifically, the reaction temperature significantly influenced crystal growth: at a low temperature, particles grew primarily in the in-plane direction, while well-crystallized layered structures formed as the temperature increased.

**Keywords:** Nanoparticles; Nanosheets; Layered metal hydroxide salts; Liquid-phase synthesis; Morphological control

ナノ粒子の液相合成では一般に、かさ高い分子や高分子を材料表面に修飾し、生成した結晶同士の物理接触を阻害することで凝集や過剰な粒子成長を抑制する。一方で、当グループでは金属水酸化物塩の合成において、2-プロペン酸のような小さな分子も保護剤とした働き、数 nm 程度のナノ粒子が生成することを見出した<sup>1)</sup>。さらに、合成したナノ粒子は溶媒和を介して安定分散し、従来の 100 倍以上まで特異的に高濃度化できることも明らかにした<sup>2)</sup>。本研究ではこの特異なナノ粒子の合成法に注目し、層状 Ni 水酸化物塩粒子の合成における反応温度や溶媒種、原料濃度、塩基試薬種をパラメーターとして変化させ、得られる試料の粒径や形態、分散性への影響を検討した。Fig. 1 に反応温度を変えて合成した試料の X 線回折(XRD)パターンを示す。低温で合成した試料は積層構造に由来する  $2\theta = 10^\circ$  未満の低角度の回折指数 003 のピークはほとんど見られず、面内方向の 110 回折ピークのみが検出された。これに対し、反応を行う温度を上げるほど、低角度の回折ピークがより顕著に現れるようになった。この結果から、層状 Ni 水酸化物塩の結晶成長速度は面方向に速く、積層方向には緩やかであることが分かった。



**Fig. 1.** XRD patterns of nickel hydroxide acrylates prepared with reaction temperature of 35–65 °C.

1) N. Tarutani *et al.*, *ACS Mater. Lett.*, **2022**, 4, 1430–1435.

2) N. Tarutani *et al.*, *J. Ceram. Soc. Jpn.*, **2023**, 131, 830–836.