2-6. Young Researchers supported by "Research Funding Support for Young Researchers"

No.	Name	Project Title
2-6-1	**Muhammad Sohail AHMAD** IINa	Polymer Grafting on Graphene Oxide: Application for Catalysis
2-6-2	**Yusuke INOMATA** FAST	Indium-Tin-Zinc Ternary Amorphous Oxide (ITZO) Nanoparticles for Acetone Detection and Elucidation of Sensing Mechanism by Operando Spectroscopy
2-6-3	**Yoshihiro SEKINE** POIE	Synthesis and Functionalization of Metal Complexes Responsive to Multiple External Stimuli
2-6-4	**Yi-Lun TSAI** FAST	Soil chemotactic signal perception and response of plant-parasitic nematodes
2-6-5	**Akira UEDA** FAST	Development of small molecule-based organic conductors with organic solvent solubility and chirality
2-6-6	**Wei XU** FAST	Antibacterial and antiviral of graphene quantum dots

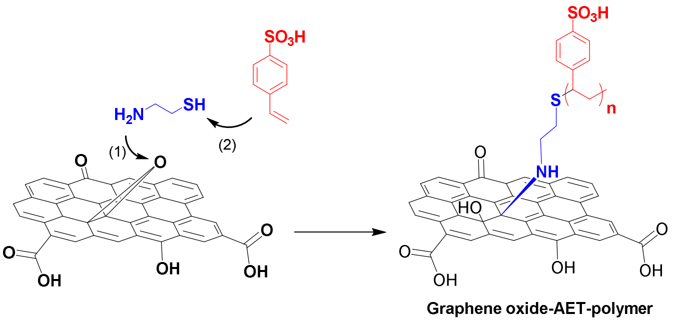
IINa：Institute of Industrial Nanomaterials
FAST: Faculty of Advanced Science and Technology
POIE: Priority Organization for Innovation and Excellence

No. 2-6-1	Polymer Grafting on Graphene Oxide: Application for Catalysis		
Name	Muhammad Sohail AHMAD		
Affiliation	Institute of industrial nanomaterials Email: sohail@kumamoto-u.ac.jp	Title	Specially Appointed Assistant Professor
Research Field	Environment-friendly technology / Advanced materials		

[Details of activities]

1. Research outline and its perspective

Graphene oxide (GO) is a versatile platform with unique properties with broad applications in electronics and catalysis. The double covalent functionalization of GO under mild conditions is an efficient approach for tuning the properties of GO. Herein, an approach involves the ring-opening reaction of epoxide by amines, followed by subsequent covalent linking of sulfonated functionalized polymer, which has been developed (Scheme 1).



Scheme 1 Covalent functionalization of GO

2. Research progress and results

We have proposed a strategy combining GO's nucleophilic epoxide ring opening reaction with the amine group in 2-aminoethanethiol (AET) (Mei et. al., *Chem. Comm.*, **2015**, 51 (81), 14981–14984) followed by thiol-ene reaction with the styrene sulfonate (Volylov et. al., *ACS Macro Lett.* **2016**, 5 (2), 199–202). This sequential approach enables the selected thiolation of GO sheets by facilitating the attachment of AET on the GO surface, thereby providing readily available thiol groups for covalent linkage with styrene (as illustrated in Scheme 1). The functionalized GO intermediates and the resulting conjugates were subjected to characterization using various techniques such as X-ray photoelectron spectroscopy (XPS), Fourier transforms infrared spectroscopy, confirming that GO was covalently functionalized. Furthermore, the functionalization confirms the removal of the surface oxygen functional groups of the GO, as confirmed by XPS (**Figure 1**). The high-resolution S2p peak of GO-AET exhibits two distinct peaks at 162.8 eV and 163.9 eV, corresponding to 2p3/2 and 2p1/2 energy levels. These peaks indicate the presence of the S−C bond in the GO-AET composites, as shown in **Figure 2**.

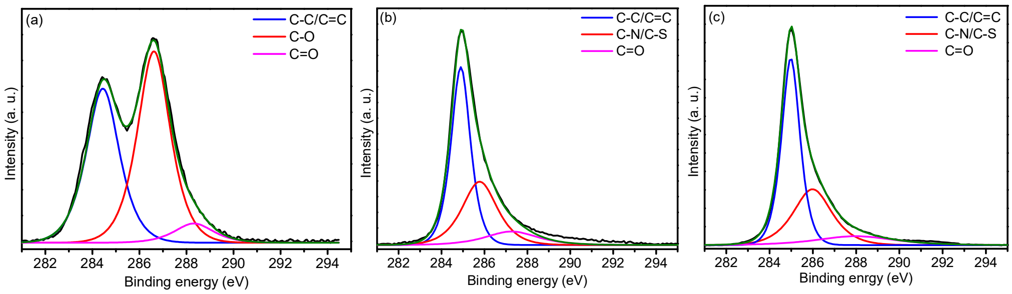


Figure 1: XPS survey of, a) C 1s of graphene oxide, (b) C 1s spectra of the GO-AET, c) GO-AET-polymer.

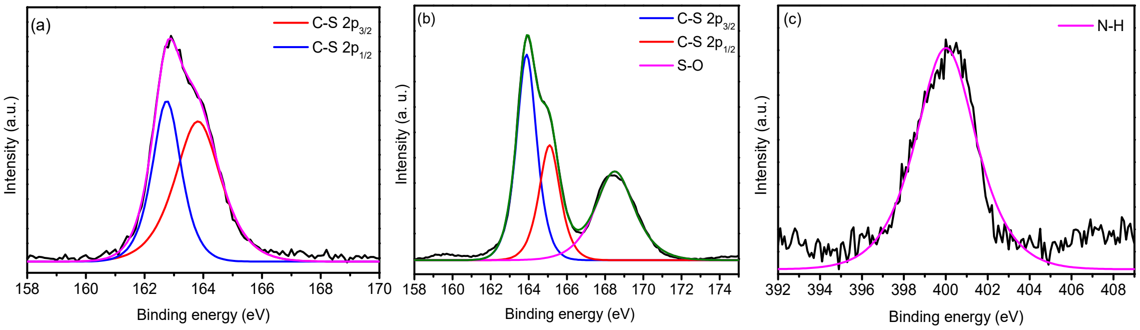


Figure 2: XPS (a) S2p survey of GO-AET, (b) S2p GO-AET-Polymer, (c) N 1s of the GO-AET.

The polymer functionalization was further characterized by XPS (**Figure 2**), revealing two main peaks at 163.6 eV and 168.5 eV, indicating the existence of sulfur. The spin-orbit coupling of the C−S covalent bond results in the observed 2p3/2 and 2p1/2 positions. The peak at 168.5 eV is due to the C−SOx species. Furthermore, the deconvolution of the N1s, peak at 400.4 eV, attributed to the NH (**Figure 2**), the results indicate that the sulfonated materials are attached to GO-AET via a linker (AET). The various GO conjugates were further characterized by FT-IR spectroscopy confirmed the functionalization of GO as shown in **Figure 3.** The peaks in the range of 1714 to 1571 cm^{-1} are due to the vibrations of C=C, C=N, and C=O, which aligns with the XPS data. The peaks observed around 1122 to 1207 cm^{-1} are assigned to the C–O and C–S/C-N bonds present in the conjugates. Furthermore, the catalytic role of the sulfonic composite attached to GO was comparatively investigated for the Ritter reaction and generate the desired product in high yield (**Scheme 2**). The remarkable activity and stability of the GO-AET-Polymer can be attributed to its substantial acid exchange capacity, which provides abundant accessible active sites. This allows it to readily interact with the $-SO_3H$ groups present on the two-dimensional graphene oxide sheets.

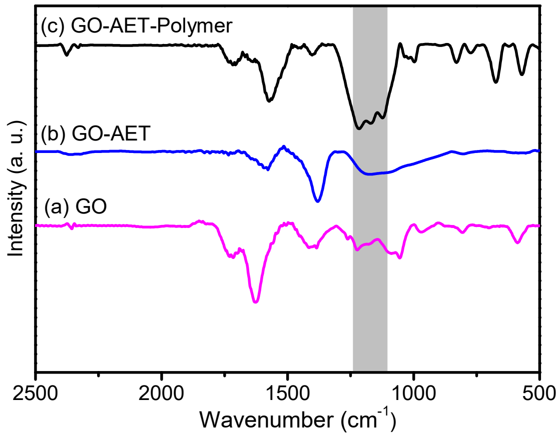
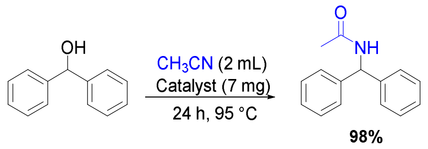


Figure 3 FT-IR spectra of various GO composite



Scheme 2 Catalytic activity of the GO-AET-Polymer in Ritter reaction

3. Research plan for the next year

For the next fiscal year, we will investigate the “Electrochemical hydrogenation of Arenes at ambient condition using Graphene based membrane reactors” and will explore the mechanism as well.

4. List of journal papers (with IROAST as your affiliation) published between April 2023 and March 2024

1. Sohail Ahmad, M., Nishina, Y., Inomata, Y., Haridiansyah, A., & Kida, T. (2024). Synergistic Functionalization of Graphene Oxide: Electrochemical Devices and Ritter Catalysis. *The Journal of Physical Chemistry C*. **Scheduled to be issued on April 2024*
2. Sohail Ahmad, M., Nagata, Y., Masumoto, K., Inomata, Y., Hatakeyama, K., Quitain, A. T., ... & Kida, T. (2024). Manganese doped graphene oxide: Selective hydrogenation catalyst for converting 5-hydroxymethyl furfural to 5-methyl furfural. *Molecular Catalysis,* 553, 113787.

3. Sohail Ahmad, M., Inomata, Y., & Kida, T. (2024). Energy application of graphene based membrane: hydrogen separation. *The Chemical Record*, 24(1), e202300163.
4. Sonda, K., Kodama, T., Wea Siga, M. D., Masumoto, K., Iwai, M., Fadil, M., ...Sohail Ahmad M*., & Kida, T. (2023). Selective Detection of CO Using Proton-Conducting Graphene Oxide Membranes with Pt-Doped SnO2 Electrocatalysts: Mechanistic Study by Operando DRIFTS. *ACS Applied Materials & Interfaces*, 15(45), 52724-52734.
5. Ashraf, M., Ali, R., Khan, I., Ullah, N., Sohail Ahmad, M., Kida, T., ... & Tahir, M. N. (2023). Bandgap Engineering of Melon using Highly Reduced Graphene Oxide for Enhanced Photoelectrochemical Hydrogen Evolution. *Advanced Materials*, 35(47), 2301342.
6. Ullah, S., Wang, Sohail Ahmad, M., Sharif, H. M. A., Liu, Q., Kida, T., ... & Qiu, J. (2023). Investigating the role of oxygen vacancies in metal oxide for enhanced electrochemical reduction of NO 3− to NH 3: mechanistic insights. *Inorganic Chemistry Frontiers,* 10(22), 6440-6488.
7. Tano, Y., Sohail Ahmad, M.*., Watase, Y., Tsugawa, T., Takase, S., Inomata, Y., ... & Kida, T. (2023). Enhancement of formic acid formation by nitrogen-doped graphene oxide nanosheets decorated with Sn nanoparticles in electrochemical CO 2 reduction. *Sustainable Energy & Fuels,* 7(16), 3964-3971.

No. 2-6-2	Indium-Tin-Zinc Ternary Amorphous Oxide (ITZO) Nanoparticles for Acetone Detection and Elucidation of Sensing Mechanism by Operando Spectroscopy		
Name	Yusuke INOMATA		
Affiliation	Faculty of Advanced Science and Technology Email: inomata@kumamoto-u.ac.jp	Title	Assistant Professor
Research Field	Advanced materials		

[Details of activities]

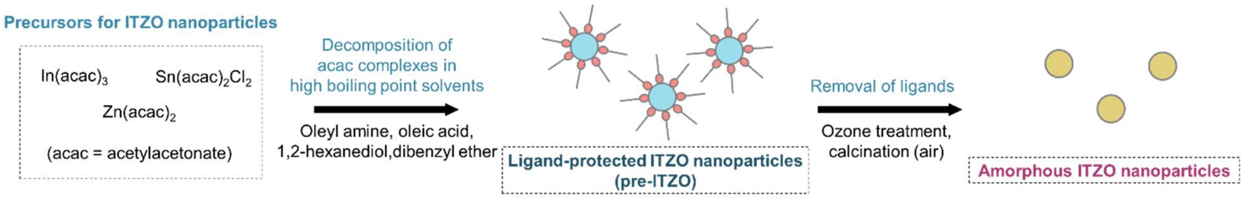
1. Research outline

Selective and quantitative detections of an acetone gas by semiconductor gas sensors have attracted much attention owing to their non-invasiveness. However, their low selectivity and high working temperature have been the task for their practical use. In this work, we report indium-tin-zinc ternary amorphous oxide (ITZO) nanoparticles for acetone sensing. ITZO shows the largest sensor responses (R_{air}/R_{gas} = 51) to an acetone gas (10 ppm) at 250°C and selective detection is confirmed. From *operando* DRIFTS observations, acetone molecules adsorb on Lewis acid sites and they are converted carboxylate intermediates followed by their decompositions during acetone detection.

2. Research progress and results

ITZO amorphous nanoparticles were prepared by a liquid phase method (***Scheme 1***). From the HADDF-STEM image of ITZO nanoparticles, amorphous atomic configurations were confirmed. We also collected elemental mapping images of ITZO nanoparticles to check the distributions of each atom. From the observations, In, Sn, Zn and O were uniformly distributed and the mapping images corresponded to the particle shape observed from their HAADF-STEM image. Thus we found that this preparation method gives ITZO amorphous nanoparticles with uniform distribution of In, Sn and Zn.

Scheme 1. Preparations of ITZO amorphous nanoparticles.



We checked the gas sensing properties (working temperature and gas selectivity) of ITZO nanoparticles and single metal oxides (SnO_2, In_2O_3 and ZnO). ITZO nanoparticles showed the selective sensor responses to 10 ppm acetone and the largest response was obtained at 250°C (R_{air}/R_{gas} = 51). Although they also showed the sensor responses to ethanol (R_{air}/R_{gas} = 24, 250°C), the responses to acetone were 2.1 times larger than that to ethanol. Pristine SnO_2 also showed the sensor responses to acetone (R_{air}/R_{gas} = 50) and ethanol (R_{air}/R_{gas} = 36). However, the working temperature at which the largest responses were obtained was 300°C and the selectivity of acetone to ethanol decreased.

Operando DRIFTS observations were also conducted to elucidate the detailed mechanism of the surface reaction during acetone sensing. DRIFT spectra were obtained under acetone gas flowing with the simultaneous observations of electrical resistance. Fifty ppm of acetone gas was introduced to observe DRIFTS spectra. ***Figure 1a*** shows the *operando* DRIFT spectra during acetone sensing (50 ppm acetone/air). A decrease in the DRIFTS peak assigned to hydroxy groups (3640 cm^{-1}) and an increase in the peak for carboxylate (acetate or formate) species (1414 cm^{-1} and 1553 cm^{-1}) were confirmed under 50 ppm acetone/air flowing (0-30 min). Time course of the change in the electrical resistance and DRIFTS areas (hydroxy group and carboxylate species) during acetone sensing (air → 50 ppm acetone/air → air) was shown in ***Figure 1b***. After introducing acetone/air, the DRIFTS areas of the hydroxy group decreased and the DRIFTS areas of carboxylate species increased with a decrease in the electrical resistance. After turning of acetone/air, recovery of the electrical resistance was confirmed and DRIFTS area of hydroxy groups slightly increased although carboxylate species moderately increased. The electrical resistance of ITZO did not recover to the original values at 250ºC. If the surface species are fully removed and the functional group completely gets recovered, the electrical resistance would be close value to the original electrical resistance because the change in the surface species was seen in DRIFTS spectra even after turning off an acetone gas. We also measured the DRIFT spectra of ITZO at room temperature under acetone gas flow. At room temperature, the DRIFT spectra peaks of ad-acetone species were confirmed and the peaks of oxidation intermediates were not seen. Therefore, there exist adsorption sites for acetone and ad-acetone species are oxidized to carboxylate species at high temperatures.

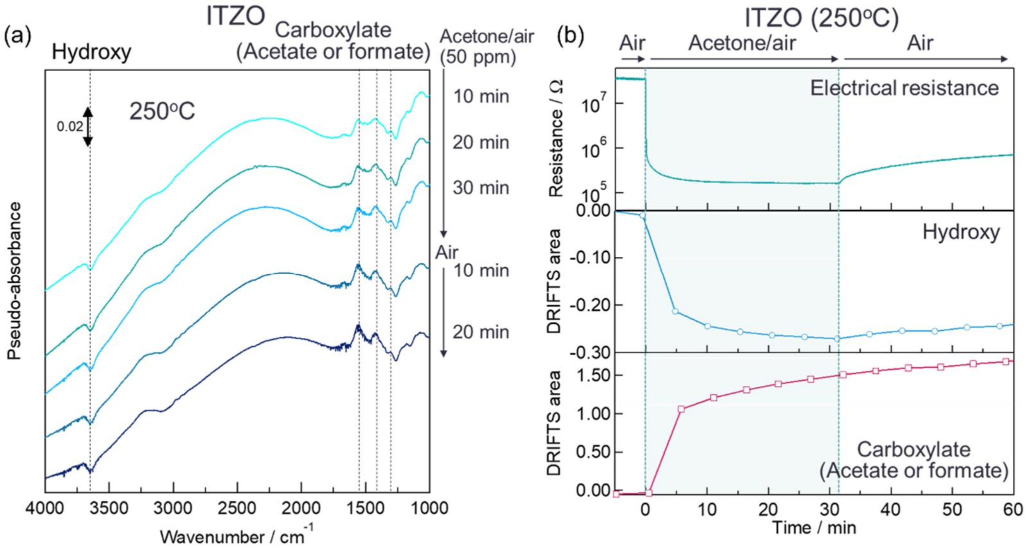


Figure 3. (a) *Operando* DRIFT spectra of ad-species on ITZO nanoparticles during acetone/ air exposure at 250ºC. Conditions: acetone/air, 50 ppm; flow rate, 100 ml/min. (b) The electrical resistance and the DRIFTS peak areas of hydroxy groups and carboxylate species versus time of gas flowing (air → 50 ppm acetone/air → air).

3. Research plan for the next year

・To improve the selectivity of sensor response to an acetone gas

4. List of journal papers

Energy application of graphene-based membrane: hydrogen separation
Muhammad Sohail Ahmad, Yusuke Inomata, Tetsuya Kida
The Chemical Record, 24(1) e202300163, 2024
https://doi.org/10.1002/tcr.202300163

Enhancement of formic acid formation by nitrogen-doped graphene oxide nanosheets decorated

with Sn nanoparticles in electrochemical CO2 reduction
Yuma Tano, Muhammad Sohail Ahmad, Yuya Watase, Tatsuki Tsugawa, Satoko Takase, Yusuke Inomata, Kazuto Hatakeyama, Shintaro Ida, Quitain Armando, Youichi Shimizu and Tetsuya Kida
Sustainable Energy & Fuels, 7(16), 3964-3971, 2023
https://doi.org/10.1039/D3SE00781B

5. List of awards, grants, and patents

n/a

No. 2-6-3	Synthesis and Functionalization of Metal Complexes Responsive to Multiple External Stimuli		
Name	Yoshihiro SEKINE		
Affiliation	Priority Organization for Innovation and Excellence Email: sekine@kumamoto-u.ac.jp	Title	Associate Prof.
Research Field	Advanced materials		

[Details of activities]

1. Research outline and its perspective

The development of functional compounds exhibiting external-stimulus-induced intramolecular electron transfers is one of the key themes in the field of materials science. Especially the external-stimuli-induced electron transfers in molecular crystals have attracted much attention because such materials are able to behave as molecular switches. In this study, the new cyanide-bridged metal complexes have been synthesized, and investigated their electronic and magnetic property (Figure). The temperature-dependent single-crystal X-ray structural analyses and magnetic data revealed that the intramolecular electron transfers between metal ions are promoted by temperature variation with the spin-state changes between diamagnetic and paramagnetic states.

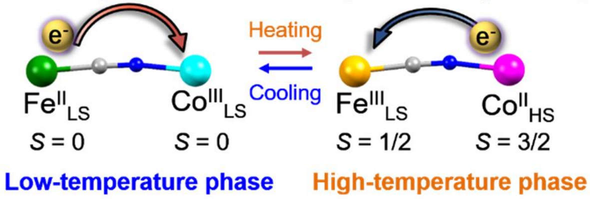


Figure. Schematic image of intramolecular electron transfers in cyanide-bridged CoFe complex

2. Research progress and results in the fiscal year

In this research, we have successfully synthesized molecular crystals based on the cyanide-bridged CoFe metal complex, exhibiting thermally driven intramolecular electron transfers. Temperature-dependence of X-ray structural analyses revealed that the bond distance around metal ions is changed, indicating that the oxidation state of constituent metal ions changed by temperature changes. These electronic state changes were also confirmed by temperature-dependent Mossbauer experiments. Temperature-dependent magnetic data revealed that the metal complex exhibited drastic magnetic changes between 200-400 K. This result suggested that this molecular crystal can be considered a magnetic switchable compound between diamagnetic ($S = 0$) and paramagnetic properties ($S = 2$) (see figure), which the electronic state was changed between [Co(II)HS-Fe(III)-LS] in the high-temperature phase and [Co(III)LS-Fe(II)LS] in the low-temperature phase, respectively. The magnetic data changed drastically at the phase transition temperatures with thermal-magnetic hysteresis, indicating the presence of a strong intermolecular interaction between the [CoFe] components. Furthermore, I got a BCSJ award for my oral presentation based on this research topic at the 1st International Conference on Spin Transition & Post conference on Phase Transition and Dynamic Properties of Spin Transition Materials (PDSTM2023).

3. Research plan for the next year

Our research this year successfully developed an external-stimuli-responsive metal complex using a cyanide-bridged metal complex. This is the first example that the supramolecular assembled methods provide switching behavior using non-responsive units. Based on this result, it is possible to replace the experimental condition, such as crystallization solvent, counter ions, etc. We plan to prepare the molecular crystals based on coordination metal complexes possessing different molecular packing architectures. Going forward, we plan to focus on developing molecular crystals that enable dielectric property switching through external stimuli and constructing reversible molecular electronic states through temperature and light control. We have obtained a guideline for the molecular design method that is useful for the development of materials that exhibit the desired external field responsiveness. In addition, by modifying the molecular design, we will also investigate the control and expression of electron transfer induced by light stimuli. Molecular arrangement control is extremely important for controlling the anisotropy of the external field-induced electron transfer in crystals, and we will investigate the molecular packing and counter ions formed based on the ligand backbone structure obtained in this study, and develop new molecular complexes.

4. List of journal papers (with IROAST as your affiliation) published between April 2023 and March 2024

N/A

5. List of awards, grants, and patents

- BCSJ Award, 1st International Conference on Spin Transition & Post conference on PDSTM, 2023, Yoshihiro Sekine
- Best Poster Award in summer school on Young Coordination Chemists' Association of Japan, 2023, Riku Fukushima, Yoshihiro Sekine, Shinya Hayami
- JSPS KAKENHI Grant-in-Aid for Early-Career Scientists, Yoshihiro Sekine
- The Sumitomo Foundation, Grant for Basic Science Research Projects, Yoshihiro Sekine
- Iketani Science And Technology Foundation, Yoshihiro Sekine
- JGC-S Scholarship Foundation, Yoshihiro Sekine

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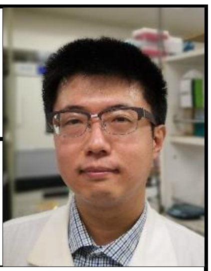
<tr><td>No. 2-6-4</td><td colspan="3">Soil chemotactic signal perception and response of plant-parasitic nematodes</td><td rowspan="2"></td></tr>
<tr><td>Name</td><td colspan="3">Yi-Lun TSAI</td></tr>
<tr><td>Affiliation</td><td>Faculty of Advanced Science and Technology
Email: tsai-yilun@kumamoto-u.ac.jp</td><td>Title</td><td colspan="2">Assistant Professor</td></tr>
<tr><td>Research Field</td><td colspan="4">Environmental bioscience / Environment-friendly technology / Strengthening resilience</td></tr>
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[Details of activities]

1. Research outline and its perspective

Plant pathogenic root-knot nematodes (RKN, *Meloidogyne incognita*) (Fig. 1, left panel) are prominent agricultural pests that infect many crop plants worldwide, and cause substantial economic loss annually. In nature, RKN are not the only soil microorganism that interact with plants. Rather, many species of bacteria and fungi, both pathogenic and symbiotic, share the same soil environment and host plants with the RKN. We are interested in how RKN interact with these microorganisms, and how these interactions affect RKN infections and pathogenesis (Fig. 1, right panel).

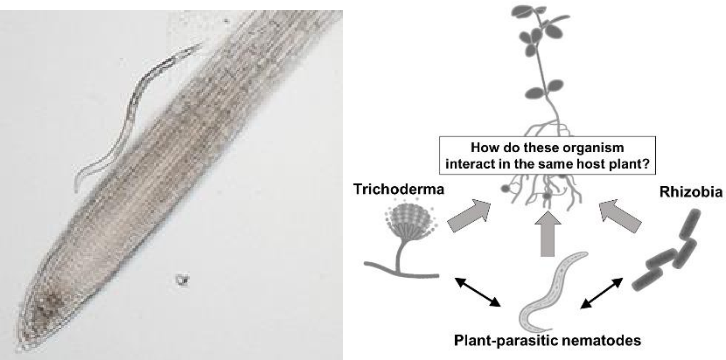


Fig. 1: Root-knot nematode (left panel) and the overall research plan (right panel)

2. Research progress and results

<u>2-1. Competitive infection behaviors between RKN and rhizobia</u>

Rhizobia refer to a group of bacteria that colonize legume plant roots and induce the formation of specialized organs known as nodules. RKN adapt a similar life style, as they also invade plant roots and induce the formation of specialized organs called galls. However, rhizobia are considered beneficial in agriculture for providing the host with organic nitrogen, whereas RKNs causes diseases and are considered pests. Since both rhizobia and RKN target the same host tissue but produce different infection outcomes, we're interested in how these organisms compete when infecting the same host plant.

Previously we were able to show that RKN strongly suppressed rhizobia (*Mesorhizobium loti*)-induced nodulation when both infect the same bird's foot trefoil (*Lotus japonicus*) host plant. We were able to more closely monitor the rhizobia infection process using a rhizobia strain with fluorescent DsRed marker, and were able to demonstrate that the early steps of nodulation, namely the rhizobial infection thread formation through the host's root hair, were blocked by RKN infection (Fig. 2).

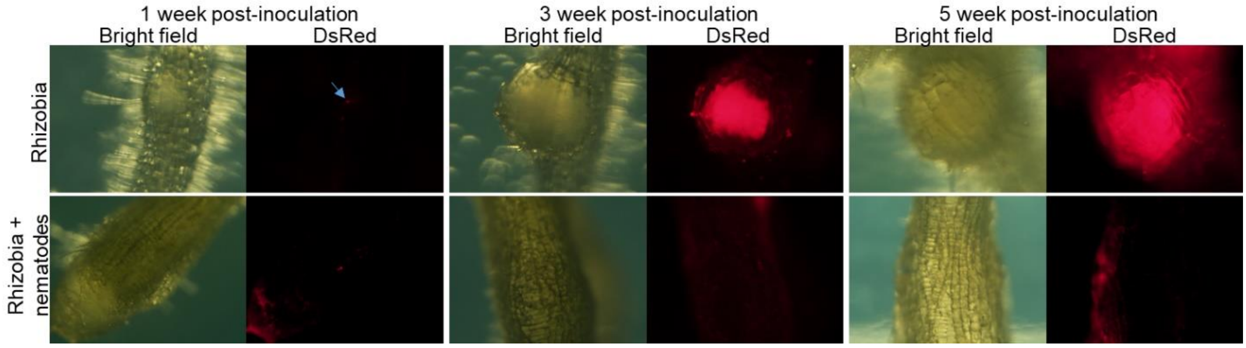


Fig. 2: DsRed-expressing rhizobia fluorescence in the presence and absence of nematode infection at 1, 3 and 5 weeks post-inoculation. Arrow denotes infection thread.

To better characterize the interactions between rhizobia and RKN, we conducted split-root assays where the root system from a single host plant is split into two compartments, and independently inoculated with RKN and rhizobia. Interestingly, RKN infection in one part of the root was able to systemically suppress rhizobia nodulation, although the suppression strength appears to weaken over distance (Fig. 3). This suggests that either RKN infection triggers the release of a certain signaling molecule that inhibits nodulation, or that RKN infection stimulates multiple signaling events that interact with each other to inhibit nodulation in a more complex fashion.

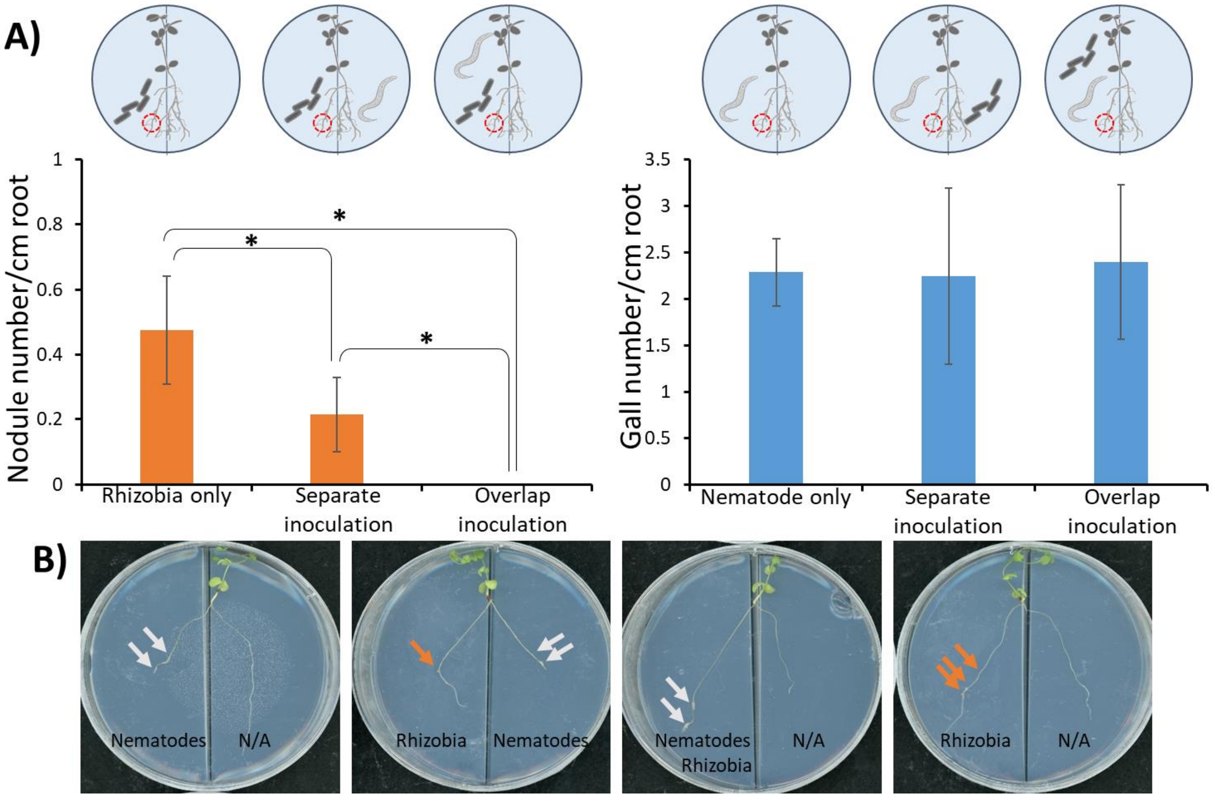


Fig. 3: (A) Nodule and gall numbers per cm root in plants co-inoculated with nematodes and rhizobia in the split-root system for 5 weeks. Averages of N = 6 ± SD are shown, * denotes significant differences, $P<0.05$, student's T-test. (B) Images of galls (blue arrows) and nodules (orange arrows) in the split-root system 5 weeks after inoculation.

<u>2-2. Identification of endophytic fungi that interact with RKN</u>

Many soil fungi are known to colonize plant roots, with some being able to promote plant growths. In order to identify such useful fungi species, we screened with soil samples collected from various locations in Kumamoto. Out of the fungi samples collected, eight were found to be competitive against pathogenic *Fusarium* fungi, making them good candidates as biocontrol reagents. Seven of these eight strains were identified to belong in the genus *Trichoderma*, which is known to contain several species with plant growth-promoting properties (Fig. 4). Interestingly, two strains, both identified as *T. atroviridae*, appear to secrete compounds that are nematocidal activities against infective RKN juveniles, while also suppressed RKN egg-hatching. These two *T. atroviridae* strains show great agricultural application potential to specifically protect crop plants from RKN infections.

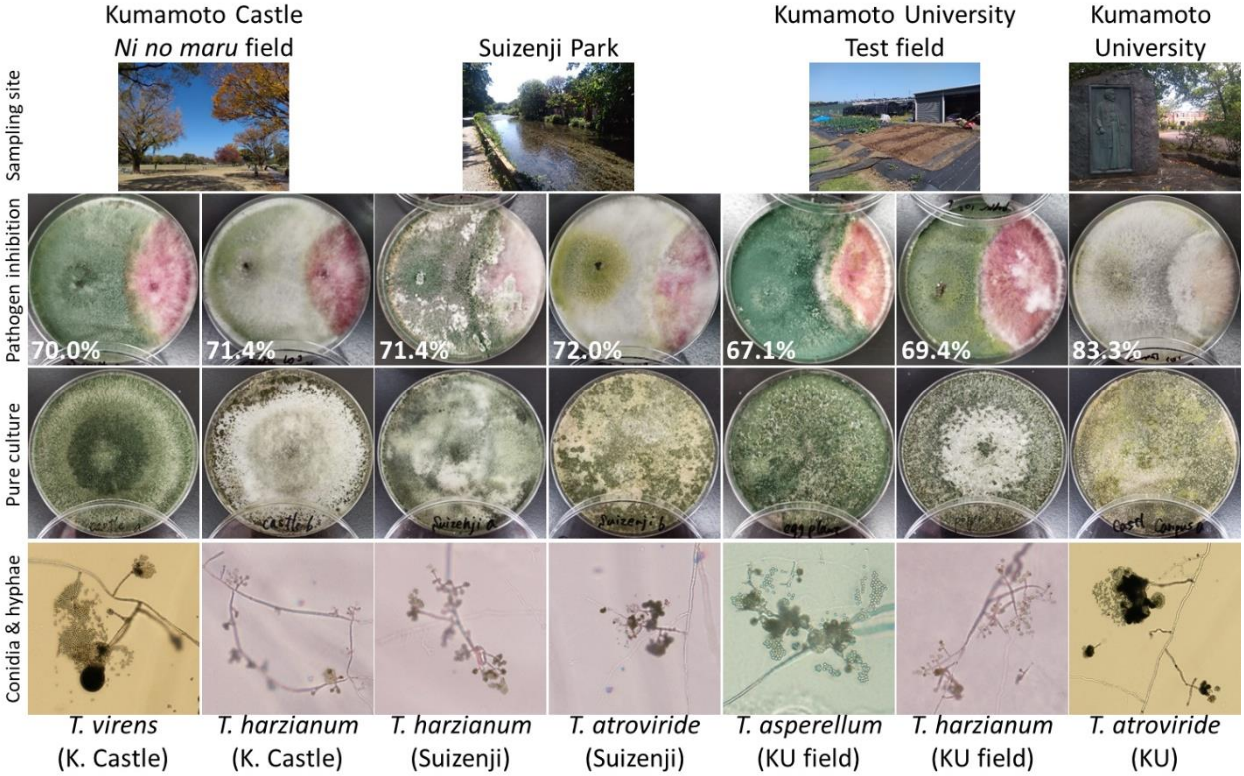


Fig. 4: Images of the sampling sites (top row), competition against pathogenic Fusarium (2nd row, *Fusarium* are the pink fungal growths on the right, percentages denote Fusarium inhibition), pure culture (3rd row), conidia and hyphae (bottom row) for the seven *Trichoderma* strains isolated, species are listed below.

3. Research plan for the next year

3-1. Systemic transcriptomic shifts induced by RKN infection

To further delineate how RKN infections suppress nodulation, particularly systemically, we are interested in examining the transcriptional shifts that occur in *L. japonicus* roots during RKN infections. In particular, we are interested to compare transcriptomic profiles of roots that have been infected by RKN, uninfected roots from the same infected plant, and roots from uninfected plants. Genes that are expressed in healthy roots from infected plants, but not in healthy plants may be involved in the systemic suppression of nodulation during RKN infection.

Several signaling molecules in *L. japonicus*, including phytohormone cytokinin and CLE signaling peptides, may be the mobile signaling molecule responsible for nodulation suppression during RKN infection. We are hoping to isolate mutants with defects in the synthesis of these signaling molecules, and test their contributions in nodulation suppression.

3-2. Characterization of RKN-antagonistic *Trichoderma* fungal species

Currently we are working on ensuring the secretion of nematicidal compounds from *T. atroviridae* is reproducible, as well as optimizing the condition to observe these effects.

Aside from secreted compounds, we are also interested in investigating whether *Trichoderma* species can influence host plant growth and RKN infection through other means. For example, we're testing whether volatile compounds produced by *Trichoderma* can affect seed germination, plant growth, and RKN resistance. In addition, we are also testing whether coating seeds with *Trichoderma* spores can facilitate their colonization of host plants, thereby enhancing their effects on the host plants and RKN infection.

4. List of papers published

(N/A)

5. List of awards, grants and patents

2023 年度ウェルシーズ一般財団法人研究寄付金，種皮分泌物の微生物誘引活性における生物肥料種子コーティング強化対策.

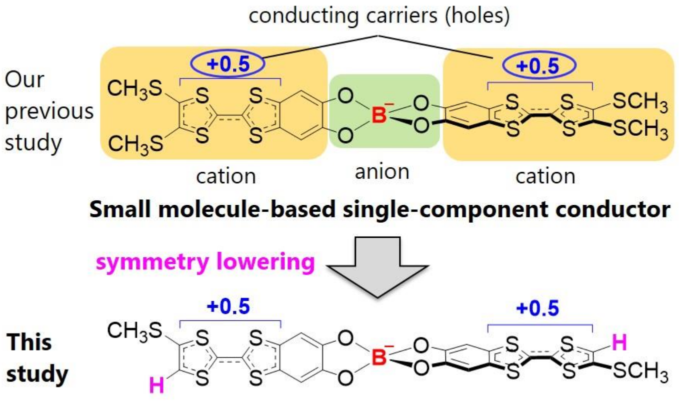
No. 2-6-5	Development of small molecule-based organic conductors with organic solvent solubility and chirality		
Name	Akira UEDA		
Affiliation	Faculty of Advanced Science and Technology Email: aueda@kumamoto-u.ac.jp	Title	Associate Professor
Research Field	Advanced materials		

[Details of activities]

1. Research outline and its perspective

Common organic materials such as paper, sugar, and naphthalene are insulators that conduct little electricity, but some organic materials such as conductive organic polymers exhibit high conductivity like metals, and have long been actively studied as electrical conductors with properties unique to organic materials, both in basic and applied aspects.

In this research, we aim to develop new possibilities and breakthroughs in the field of organic conductors by means of original molecular design and material development, focusing on small molecule-based organic conductors for which precise molecular design is possible (see figure).

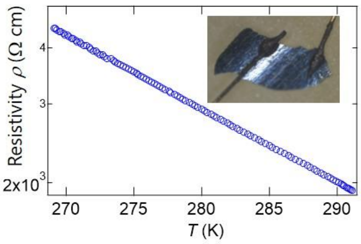


Aiming to *improve solubility* and *introduce axial chirality*

2. Research progress and results in the fiscal year

As shown in the upper right figure, we have previously succeeded in the development of small molecule-based single-component conductors by our original molecular design of connecting two cation moieties through an anion species (supported by IROAST in FY2021–2022). On the basis of this study, in this fiscal year (FY2023), we have aimed to lower the symmetry of this cation-anion-cation triad molecule by chemical modifications, thereby imparting organic solvent solubility and axial chirality to this type of small molecule-based organic conductors for the first time and consequently opening a new field of organic conductor research.

After various examinations of the design and synthesis of such molecules, we have successfully obtained a black solid (see right figure) composed of an axially chiral derivative (see upper right figure) in which two hydrogen atoms are introduced instead of the two CH_3S groups in the original molecule. Similar to the previous material, this solid is stable in air at room temperature. On the other hand, unfortunately, it showed no solubility in common organic solvents, although the lowered symmetry of the molecule is expected to improve solubility. However, we see that this black solid has extremely high conductivity (10^{-4} S/cm) among conventional small molecule-based single-component solids (e.g. the conductivity of naphthalene is about 10^{-18} S/cm). These results demonstrate that our molecular design of connecting two cation moieties through an anion species is a reliable way to obtain highly conducting small molecule-based organic materials with various functions including chirality.



3. Research plan for the next year

As shown above, we have found that the material obtained in FY2023 was not soluble in organic solvents but has axial chirality and sufficient conductivity. Therefore, in the next year (FY2024), we will perform optical resolution of this material to obtain its enantiopure crystals, because such enantiopure crystals without space-inversion symmetry have the possibilities to exhibit interesting chiral physical properties such as nonreciprocal conductivity and chiral magnetism. It should be noted that axial chirality inherent in this system might give more significant chiral effects than point chirality used in the conventional chiral molecular crystalline materials. In order to elucidate the structure-property relationship in detail, the crystal structure analysis and the calculations of the intermolecular transfer integrals and band structures are also needed. Furthermore, to provide this type of materials with solubility, elongation of the alkyl substituents, for example, substitution of the methylthio (CH_3S) groups in the present molecule to ethylthio (CH_3CH_2S) or propylthio ($CH_3CH_2CH_2S$) ones, should be examined. After obtaining soluble small molecule-based organic conductors, the fabrication of their thin film devices and the evaluation of the properties will be performed, in order to explore new electronic properties and functionalities of small molecule-based organic materials.

4. List of journal papers (with IROAST as your affiliation) published between April 2023 and March 2024

Not applicable

5. List of awards, grants, and patents

· Grant-in-Aid for Transformative Research Areas (A) 23H04035, FY2023-2024 (Principle Investigator), Direct Cost: ¥6,000,000, “Zwitterionic neutral radical-based strongly correlated electron systems with high-dimensional condensed conjugation”

·Grant-in-Aid for Scientific Research (C) 23K04692, FY2023-2025 (Principle Investigator), Direct Cost: ¥3,700,000, “Modulation of band filling and exploration of novel electronic phases in purely organic neutral radical solids”

No. 2-6-6	Antibacterial and antiviral of graphene quantum dots		
Name	Wei XU		
Affiliation	Faculty of Advanced Science & Technology Email: xuwei@kumamoto-u.ac.jp	Title	Assistant Professor
Research Field	Biotechnology & healthcare technology		

[Details of activities]

1. Research outline and its perspective

Graphene quantum dots (GQDs), nanostructures of graphene with non-zero band gap show unique optical and electronic properties. However, most of reported GQDs are water-soluble, which limits their applications as antimicrobial materials. We found a simple method to synthesize water-insoluble hydrophobic GQDs, and we measured their antibacterial and antiviral activities. In addition, it will be easy to hybrid hydrophobic GQDs easily and hydrophobic polymer. We further evaluated the their antibacterial and antiviral activities of GQDs contained polymer films.

2. Research progress and results in the fiscal year

To investigate the mechanism of antibacterial and antiviral activities of GQDs, we incubated bacteria with GQDs and then performed TEM observation. After the incubation, process of fixation and dehydration of bacteria were performed. As shown in Fig.1, we observed that GQDs were significantly adhered on the surface of bacteria, whereas hydrophilic GQDs are not. We suggested that the hydrophobicity of GQDs improved the adhesion to bacteria, resulting inhibiting the activity of bacteria. The adhesion was due to the hydrophobicity of bacterial cell surface caused hydrophobic-interactions between GQDs and bacteria.

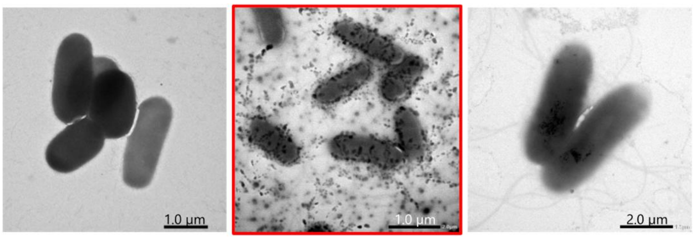


Fig.1. TEM images of bacteria (left), incubated with hydrophobic GQDs (middle), incubated with hydrophilic GQDs (right).

Biodegradable polymers are widely used in biomedical and pharmaceutical fields. They can be roughly divided into synthetic and natural biodegradable polymers. For synthetic biodegradable polymers, in this study we used polycaprolactone (PCL) and poly(lactic-co-glycolic acid) (PLGA) to prepare biodegradable polymer films. The amorphous segments and molecular of polymers that is known for its high degree of crystallinity. The amorphous segments and molecular weight determine its degradation rate and influence its mechanical properties. Whereas, for natural polymers, silk fibroin was used to prepare polymer film. Silk fibroin (SF) is an attractive natural protein produced by the silkworm (Bombyx mori) for biomedical application because of its permeability to oxygen and water, controlled biodegradability, good cell adhesion, low inflammatory response, and high tensile strength.

For evaluation of antibacterial activity, gram-negative bacteria, *E. coli* was cultured with GQDs-contained polymer films and measured concentration of the bacteria in the medium within 6 h. As shown in Fig.2, only polymer films did not have antibacterial activity. When mixing with GQDs, the hybrid film exhibited antibacterial activity. In addition, due to the different property of polymers, they showed different antibacterial activity. PLGA+GQDs showed a lower activity was thought polymer PLGA is hard polymer, resulting a slow release of GQDs. Whereas, PCL is a rubber-like flexible polymer, it released GQDs rapidly, resulting a higher antibacterial activity. SF, SF consists of a heavy (H) chain of ~390 kDa and a light (L) chain of ~25 kDa connected by a disulfide bond at the C-terminus of the H chain, forming an H−L complex. The structure of the H-chain consists of 12 hydrophobic domains scattered with 11 hydrophilic domains. The H-chain forms β-sheet structures and is the main component of its mechanical properties. Therefore, amount of GQDs was released along with SF, exhibited antibacterial activity.

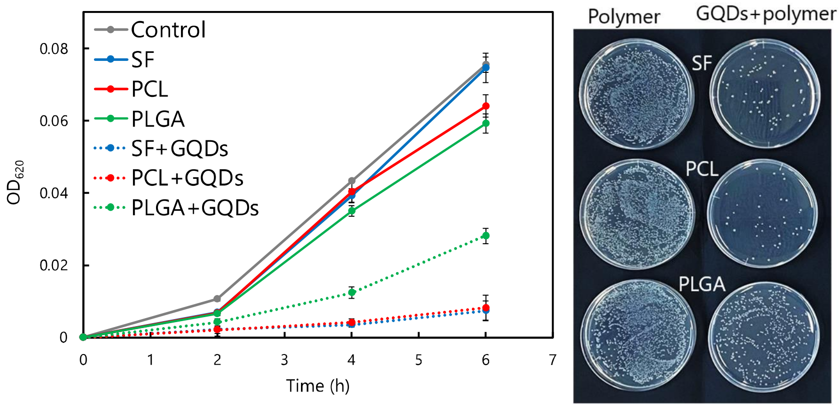


Fig.2. Antibacterial activity of GQDs-contained polymer films.

3. Research plan for the next year

Although GQDs showed antibacterial activity. However, it is non-specify. In addition, we found that GQDs induced cytotoxicity. Therefore, next year, I will coat GQDs with bacterial membrane vesicles (MVs, Fig.3). MVs contain lipids, bioactive proteins, nucleic acids, and metabolites, play important roles in microbial physiology, and have great potential for immunotherapeutic applications, such as bacterial vaccine and cancer immunotherapy. Therefore, GQDs@MVs would be expected to have selective antibacterial activity and low cytotoxicity.

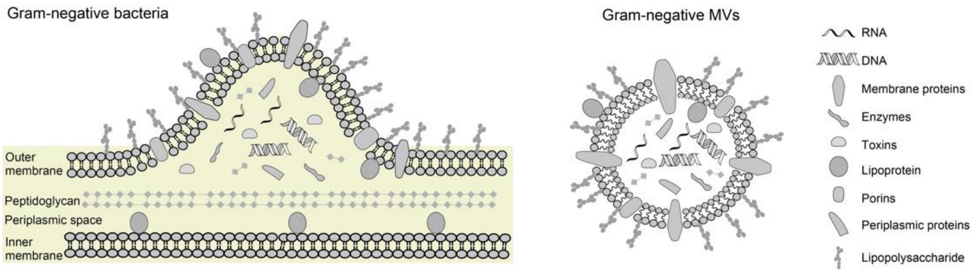


Fig.3. Structure of bacterial membrane vesicles.

4. List of awards, grants, and patents

None

5. List of journal papers (with IROAST as your affiliation) published between April 2022 and March 2023.

None