2-3. IROAST Postdoctoral Researchers

No.	Name	Project Title
2-3-1	**Jonas Karl Christopher Nuevas AGUTAYA**	Elucidation of the gas sensing mechanism of semiconductor metal oxides by a combined DRIFTS and DFT approach
2-3-2	**Nobleson KUNJAPPY**	Characterization of Noise Components in Pulsar Timing Signals for Enhanced Gravitational Wave Detection
2-3-3	**Prafulla Bahadur MALLA**	Seismic performance of shear walls with low bond ultimate high strength bars under multiple reverse cyclic loading induced by long period ground motion earthquake
2-3-4	**Mohammad Atiqur RAHMAN**	Perovskite, metal oxide nanosheet, proton conductivity, fuel crossover, Proton Exchange membrane fuel cell
2-3-5	**Reetu Rani**	Environmental applications of Metal Organic Frameworks

No. 2-3-1	Elucidation of the gas sensing mechanism of semiconductor metal oxides by a combined DRIFTS and DFT approach.8			
Name	Jonas Karl Christopher Nuevas AGUTAYA	Title	Postdoctoral Researcher	
Affiliation	IROAST Email: jnagutaya@chem.kumamoto-u.ac.jp			
Research Field	Advanced materials			

[Details of activities]

1. Research outline and its perspective

This research employs diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to elucidate the gas sensing mechanism of semiconductor metal oxide (SMOX)-based sensors. To complement the experimental results, calculations based on the density functional theory (DFT) are also performed. This study will provide a chemist's perspective in modeling gas sensing for the development of better sensors.

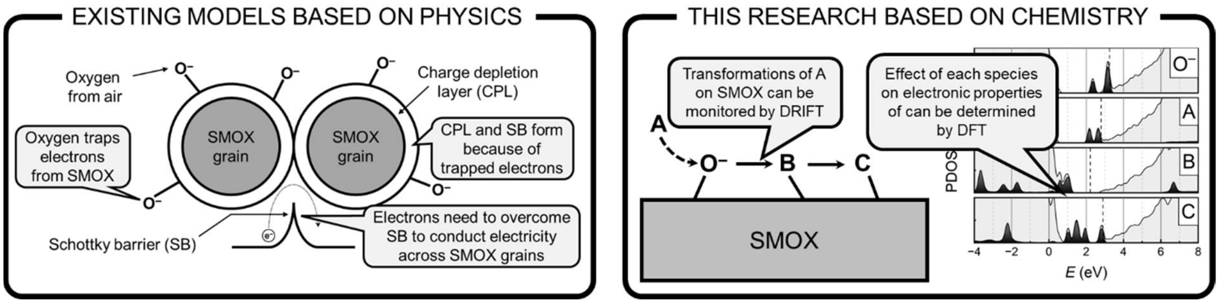


Figure 1. Models for the gas sensing mechanism of SMOX based on physics (existing models) and chemistry (this research)

2. Research progress and results in the fiscal year

[*Published*] DFT calculations were performed to identify the role of platinum in the detection of carbon dioxide by proton-conducting graphene oxide membranes with Pt-doped SnO_2. The calculations revealed that platinum on SnO_2 can serve as an effective site for the adsorption of carbon monoxide prior to its oxidation at the graphene oxide surface. The form of Pt was also shown to be an important factor in the adsorption of carbon monoxide with Pt-adsorbed SnO_2 as its more preferred site than Pt-substituted SnO_2. The optimized structures of Pt-modified SnO_2 with adsorbed CO are shown in Figure 2 with the corresponding adsorption energies (more negative means better adsorption). These results were correlated with temperature-programmed desorption to explain how the higher concentration of adsorbed Pt in the in-house Pt-doped SnO_2 was responsible for its higher adsorption capacity than the commercial catalyst.

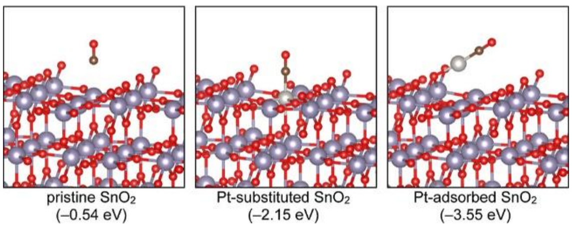


Figure 2. Optimized structures of carbon monoxide on the surface of SnO_2 in different configurations. The adsorption energies are shown in parentheses. Legend: blue circle solid: Sn; red circle solid: O, brown circle solid: C; and gray circle solid: Pt.

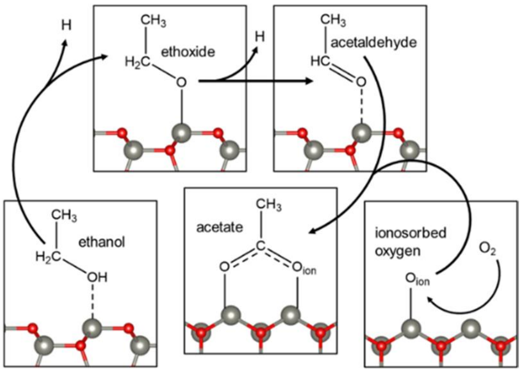


Figure 3. Proposed pathway for the conversion of ethanol over the ZnO (10$\bar{1}$0) surface

[*Accepted as of 2024 Feb 2*] DFT calculations were also performed in another study on the ethanol sensing mechanism of ZnO nanorods. Comparing the dimensions of the optimized structure of ZnO with the interatomic distances and angles measured by high-angle annular dark field scanning transmission electron microscopy, the (10$\bar{1}$0) plane of ZnO was determined to be the dominant surface in the sensing layer. Using DRIFTS and product gas analyses, the adsorbates and products that were formed from ethanol during its detection were identified. Based on these experimental data, a pathway for the conversion of ethanol over ZnO(10$\bar{1}$0) was proposed as shown in Figure 3.

To determine the effect of each adsorbed species on the electronic properties of ZnO, calculations involving projected density of states (PDOS) were also performed. The PDOS plots in Figure 4 show the energy levels introduced by each species in the reaction pathway. In the case of adsorbed oxygen (O_{ion}) and ethoxide, the energy levels within the band gap of ZnO and intersecting the Fermi level (dashed line) indicated an increase in the electrical resistivity of ZnO. In the case of acetaldehyde and acetate, on the other hand, the shift of these energy levels away from the Fermi level and some into the conduction band of ZnO indicated a decrease in its electrical resistivity. From sensor performance measurements, the exposure of the ZnO nanorods to ethanol resulted in a decrease in its electrical resistance. Therefore, the dehydration of ethanol to acetaldehyde and further oxidation of acetate are proposed to be key reactions in the detection of ethanol by the ZnO nanorods.

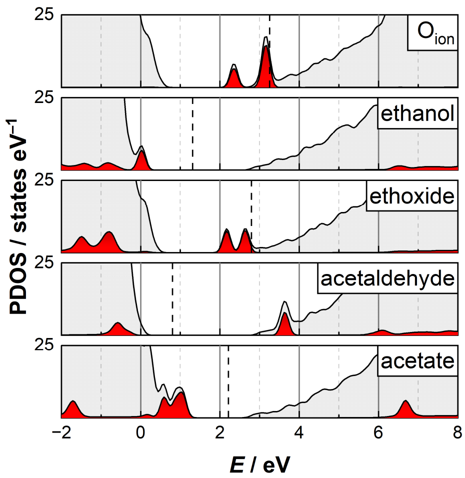


Figure 4. Total density of states (DOS, gray region) and the projected contribution of the adsorbates (PDOS, red region) on ZnO(10$\bar{1}$0)

3. Research plan for the next year

The adsorption and PDOS calculations will be extended to other systems such as SnO_2 and WO_3, both in pristine and noble-metal modified configurations, as well as multi-metal SMOX like zinc-indium-tin oxide. The interaction of these materials to gases other than ethanol and carbon dioxide (*e.g.*, acetone, methane) will also be evaluated. An additional method known as the nudged elastic band, will also be performed to generate the intrinsic reaction coordinate for the surface reactions (Figure 5) and determine the most viable reaction pathway.

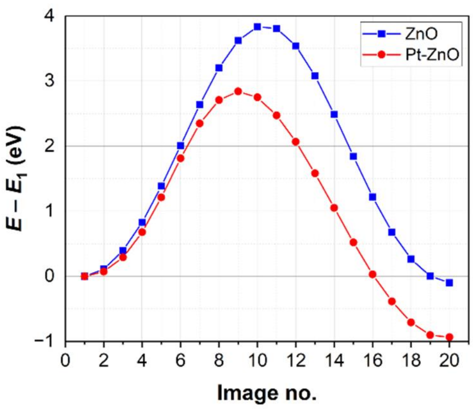


Figure 5. Sample graph of the intrinsic reaction coordinate

4. **List of journal papers published between April 2023 and March 2024**
    - K. Sonda, T. Kodama, M. D. Wea Siga, K. Masumoto, M. Iwai, M. Fadil, M. S. Ahmad, **J. K. C. N. Agutaya**, Y. Inomata, A. T. Quitain, A. Hardiansyah and T. Kida, "Selective Detection of CO Using Proton-Conducting Graphene Oxide Membranes with Pt-Doped SnO2 Electrocatalysts: Mechanistic Study by Operando DRIFTS," *ACS Appl. Mater. Interfaces*, 2023, **15**, 52724–52734.

5. **List of awards, grants, and patents**
    - None

6. **Other activities**
    - **[Participation in conferences]**

        a. **Jonas Karl Christopher Agutaya**, Takeshi Shinkai, and Tetsuya Kida. "Elucidation of the ethanol gas sensing mechanism of ZnO using a combined DRIFTS and DFT approach". *49th International Congress on Science, Technology and Technology-Based Innovation (STT49)*. Songkhla, Thailand. 2024 January 23–25.

        b. **Jonas Karl Christopher N. Agutaya**, Yūki Shimada, Yūsuke Inomata, and Tetsuya Kida. "DRIFTS/DFT study of the CO sensing mechanism of Pd-loaded SnO_2". *18^{th} International Conference on Nano/Micro Engineered and Molecular Systems (IEEE-NEMS 2023)*. Jeju, Korea. 2023 May 14–17.

Taken during the STT49 (Thailand)

Taken during the IEEE NEMS 2023 (Korea)

No. 2-3-2	Characterization of Noise Components in Pulsar Timing Signals for Enhanced Gravitational Wave Detection			
Name	Nobleson KUNJAPPY	Title	Postdoctoral Researcher	
Affiliation	IROAST Email: nobleson@kumamoto-u.ac.jp			
Research Field	Data science and AI			

1. Research outline and its perspective

Low-frequency gravitational wave (GW) detection using pulsar timing is a cutting-edge field at the intersection of astrophysics and data science. Pulsars, dense neutron stars emitting regular radio pulses, serve as natural cosmic clocks. Understanding their timing variations due to gravitational waves offers insights into cosmic events like black hole mergers. However, the accuracy of this method is challenged by noise sources within pulsar signals, necessitating a thorough investigation to enhance GW detection sensitivity.

The primary goal of this research project is to comprehensively characterize and mitigate noise elements in pulsar timing signals. By identifying and understanding the various noise sources, including intrinsic pulsar timing noise, interstellar medium effects, and instrumental artifacts, we aim to develop advanced signal processing techniques. These techniques will enable the effective removal of noise while preserving gravitational wave signals, ultimately improving the signal-to-noise ratio crucial for robust and high-confidence GW detection using pulsar timing arrays.

2. Research progress and results in the fiscal year

The research progresses through two parallel streams:

1. Investigating the impact of noise processes using low-frequency data observed by Indian Pulsar Timing Array. During a collaboration meeting held in Chennai, India, in the first week of February, various methods for understanding noise contributions were deliberated upon, and implementation is underway.

2. Combining data from multiple radio telescopes across different PTAs for a select sample of pulsars is done. Initial runs of noise analysis on this dataset are currently under discussion, aiming to enhance our understanding of noise characteristics and their effects on gravitational wave detection using pulsar timing.

3. Research plan for the next year

We are currently working to implement sophisticated methods for data analysis, building upon the insights gained from previous discussions. Our focus will be on testing the efficacy of these models in accurately characterizing and mitigating noise elements within pulsar timing signals. Additionally, the plan to participate in another international collaboration meeting in Italy later this year, where we will delve deeper into the practical implementation of these noise models. This meeting will specifically address the application of noise models to the remaining 100 pulsar datasets, paving the way for a comprehensive analysis across a larger sample size.

The ultimate goal is to refine our techniques to a level where they can reliably contribute to the detection of gravitational waves using pulsar timing arrays. Through iterative refinement and collaboration, we aim to enhance the sensitivity and accuracy of our methods for robust GW detection.

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

   1. Low-frequency pulse-jitter measurement with the uGMRT I: PSR J0437−4715. Accepted for publication by the **Publication of the Astronomical Society of Australia (PASA)**.

   2. Comparing recent PTA results on the nanohertz stochastic gravitational wave background. Accepted for publication in the **The Astrophysical Journal (ApJ)**

5. **List of awards, grants, and patents**

   None

No. 2-3-3	Seismic performance of shear walls with low bond ultimate high strength bars under multiple reverse cyclic loading induced by long period ground motion earthquake			
Name	Prafulla Bahadur MALLA	Title	Postdoctoral Researcher	
Affiliation	IROAST Email:malla@kumamoto-u.ac.jp			
Research Field	Strengthening resilience			

[Details of activities]

1. Research outline and its perspective

Reinforced concrete (RC) shear walls are widely accepted cost-effective measures for resisting lateral loads and controlling inter-story drift within specified code limits. RC walls undergo significant inelastic deformation, effectively dissipating seismic energy while ensuring life safety performance. This study investigates use of low bond ultimate high strength (LBUHS) rebars as longitudinal bars in the shear walls for development of resilient shear wall member. The RC walls were tested under multiple-reversed lateral cyclic (MRC) loads, simulating the effects of long-period strong ground motion earthquakes (LPGM) to investigate their seismic safety.

2. Research progress and results in the fiscal year

The research work to study the seismic performance of RC walls with use of low bond ultimate high strength (LBUHS) bars has been concluded. All together 6 specimens were prepared with an effective height of 1350 mm, a width of 600 mm, and a thickness of 150 mm, resulting in an aspect ratio of 2.25. The detailing and percentage of reinforcement is shown in Figure 1 and Table 1, respectively. The parameters included in the tests are: (1) type of reinforcing bars ordinary and LBUHS (2) axial load ratio (3) Type of loading Normal cyclic loading and MRC, and (4) percentage of confined stirrups.

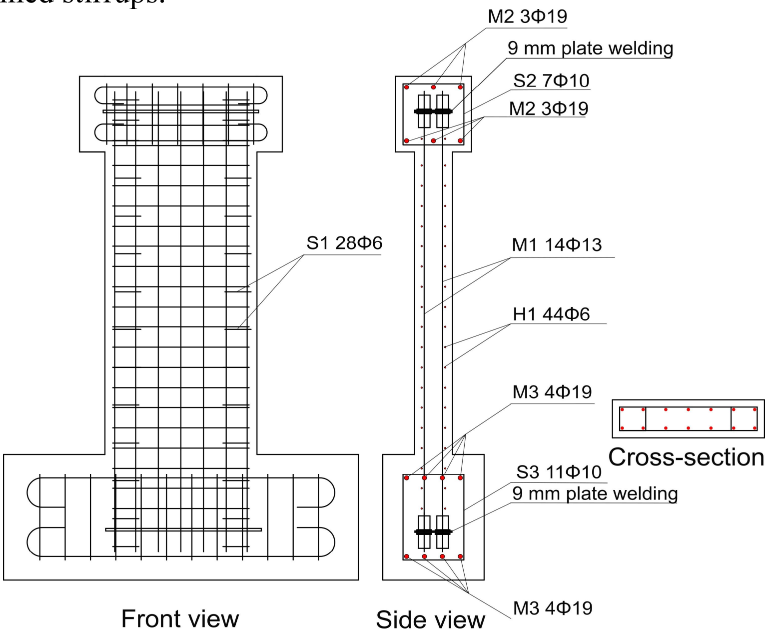


Figure 1 Detailing of reinforcements of the wall

Table 1 Reinforcing bars of shear wall

Name	Axial load	Boundary section		Vertical mid bar		Horizontal bar		Confined stirrup		Load type
		bar	p_v	Bar	p_{mid}	Bar	p_h	Bar	p_s	
	kN		%		%		%		%	
SW1	360	D13	2.68	D13	0.88	D6	0.50	**D6**	0.88	NC
SW2	360	D13	2.68	D13	0.88	D6	0.50	D6	0.88	MRC
SW3	360	U12.6	2.52	U12.6	0.83	U7.1	0.71	U7.1	0.88	NC
SW4	360	U12.6	2.52	U12.6	0.83	U7.1	0.71	U7.1	0.88	MRC
SW5	792	U12.6	2.52	U12.6	0.83	U7.1	0.71	U7.1	0.88	MRC
SW6	360	U12.6	2.52	U12.6	0.83	U7.1	0.71	U7.1	0.44	MRC

The shear wall with LBUHS bars showed higher strength and self-centering behavior as compared to ordinary reinforcing steel bars. Shear wall with ordinary reinforcing steel bars showed higher energy dissipation than the shear wall with LBUHS bars. The shear wall with LBUHS bar showed slightly higher stiffness after 0.75% drift. Under MRC loading, yield load, maximum load, and ultimate failure occurred at lower drift compared to NC loading. The noticeable variation in the load-drift curve is observed after 2% drift. The load-drift curve's envelope exhibits dependency on the load path, with multiple repetitions of loading under MRC, the shear wall experiences greater strength deterioration. The residual drift increases after 0.75% drift in MRC loading compared to NC loading. This observation highlights the vulnerability of shear wall structures to collapse during LPGM events at lower intensity. The effect of axial load is also pronounced. Under the high axial load , there is shear failure, with sudden collapse of the shear wall.

One conference paper has been published and two has been submitted on the basis of experimental work. Currently, SCI paper have been in progress and will be submitted at the end of April, 2024.

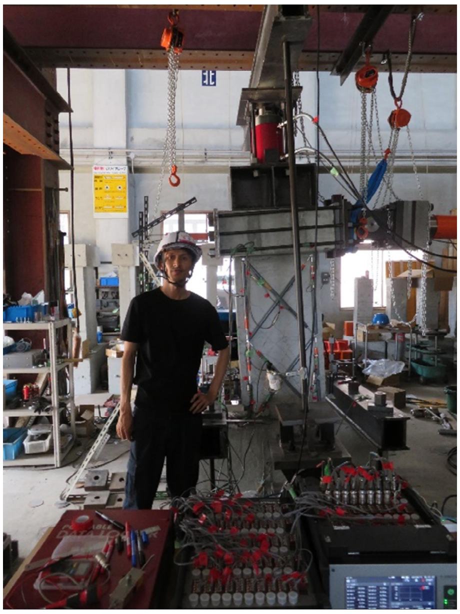


Figure 2 Experiment of shear wall

<u>Journal paper submitted</u>

1. Gaochuang Cai, Yue Wen, **Malla Prafulla**, Takashi Fujinaga and Amir Si Larbi. Effect of axial load and shear span on seismic performance of CFT columns reinforced with end-fixed ultra-high strength rebars. Bulletin of Earthquake Engineering.(IF 4.6, 2022)
2. **Prafulla B. Malla**, Gaochuang Cai, Yuan He, Yue Wen and Chen Xie. Experimental Investigation on Seismic Performance of Reinforced Concrete Shear Walls Under Long-Period Earthquakes Via Quasi-Static Multiple Reversed Cyclic Loading. Bulletin of Earthquake Engineering.(IF 4.6, 2024)

Journal paper under preparation

1. **Malla Prafulla** and Gaochuang Cai. Seismic performance of shear wall with low bond high strength bars under multiple reverse cyclic loading induced by long duration earthquake. Bulletin of Earthquake Engineering.(IF 4.6, 2024)

Conference paper published

1. **MALLA Prafulla**, CAI Gaochuang, WEN Yue, HE Yunjian and XIE Cheng, " Seismic Performance of Shear Walls under Multiple Reverse Cyclic Loading Induced by Long Duration Earthquake" Kyushu conference, Kagoshima, 2024.
2. WEN Yue, CAI Gaochuang and **MALLA Prafulla**, " Seismic behavior of resilient column with ultra-high strength rebars under multiple cyclic loads", The 16th Japan Earthquake Engineering Symposium, Yokohama, 2023

Conference paper submitted

1. MALLA Prafulla, CAI Gaochuang, HE Yunjian, WEN Yue and XIE Cheng, " Effect of Axial load ON SEISMIC performance of shear walls with low bond ultimate high strength bars: an experimental study", Kyoto conference, 2024.
2. CAI Gaochuang, **MALLA Prafulla**, HE Yunjian, WEN Yue, XIE Cheng "Proposal for a HSR RC shear wall to resist strong earthquakes with LPGMs: an experimental study", world conference on earthquake engineering 2024 Italy, Milan, 2024.
3. WEN Yue, CAI Gaochuang, KIKUCHI Hayato and **MALLA Prafulla**, " Seismic behavior of resilient column with ultra-high strength rebars under multiple cyclic loads", World Conference on Earthquake Engineering 2024 Italy, Milan, 2024.

3. Research plan for the next fiscal year

The research work on CFST frame is currently under progress. The research work is in design phase. There will be altogether 5 specimens with two types of beam-column joint: (1)Through Diaphragm type and (2) Through beam type. The experimental specimen is shown in Figure 3.The different parameters are included in the test are axial load ratio, loading type and D/t ratios. The experimental specimen is shown in Figure 3.

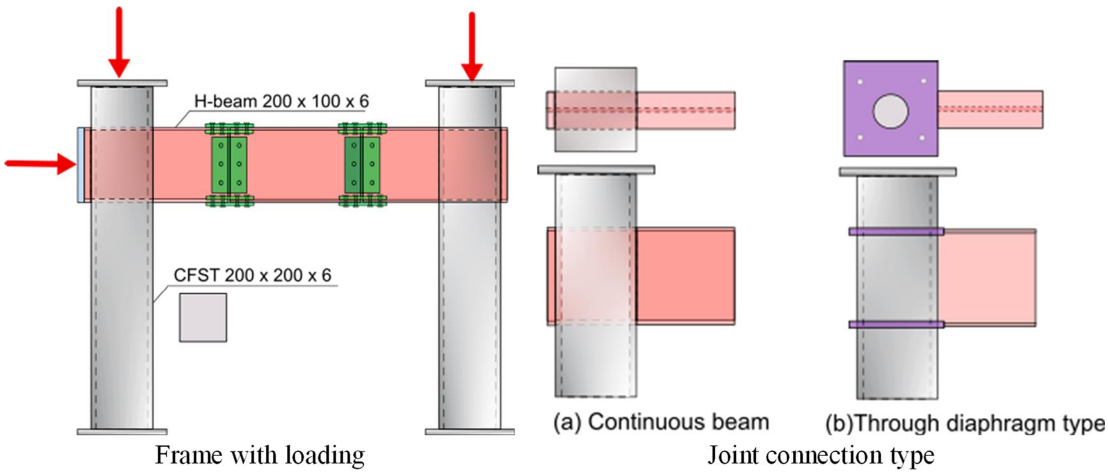


Figure 3 Experimental work for CFST column-steel beam

4. **List of journal papers (with IROAST as your affiliation) published between April 2023 and March 2024**
    1. Cai, G., Fujinaga, T., Si Larbi, A., Wen, Y., & **Malla, P. B**. "Cyclic behavior of RCFT columns with large D/t ratio steel tubes: Effect of reinforcement arrangement." Bulletin of Earthquake Engineering 21.9 (2023): 4565-4588.

5. **List of awards, grants, and patents**
    1. Ohata Foundation Research grant, Project title: Seismic performance and AI-based evaluation method of SRC square columns subjected to multiple repeated seismic loads, FY2022, Total budget: 2,000,000Yen. PI: Dr. G. CAI, Research co-investigator: **Malla Prafulla**
    2. Grants-in-Aid for Scientific Research, Category C, Project Number: 23K04120, Fiscal Years 2023-2026, " **Development of a new low- and medium-rise CFST structural system using steel-concrete mechanical behavior of joints**," Principal Investigator (PI): Dr. T. Fujinaga**,** Researcher: Dr. G. Cai and **Malla Prafulla**, Total budget: 4,680,000 JPY**.**
    3. Grants-in-Aid Early Career Scientists, Project Number: 24K17393, Fiscal Years 2024-2025, **" Seismic Performance and Evaluation of Hybrid Frame with CFST column-continuous Beam Joints**," Principal Investigator (PI): Dr. Prafulla Bahadur Malla, Total budget: 3,380,000 JPY.

No.2-3-4	Perovskite, metal oxide nanosheet, proton conductivity, fuel crossover, Proton Exchange membrane fuel cell		
Name	Mohammad Atiqur RAHMAN	Title	Postdoctoral Researcher
Affiliation	IROAST Email: atiqur@kumamoto-u.ac.jp		
Research Field	Advanced materials		

1. Research outline and its perspective

The demand for clean and sustainable energy resources has been soaring over the last few decades with the worldwide energy demand. Both these issues are obviously burning problems in terms of environmental pollution and increases in the average temperature of this planet. For this reason, development of clean and maintainable energy systems and advanced energy storage devices have become more significant than ever. In response to this, fuel cell, where electric energy is produced from chemical energy through an electrochemical reaction find interests by the researcher to fulfill the growing energy demands of newly emerging applications. Commercially Nafion has been used as electrolyte in fuel cell. Although they provide high proton conductivity, but strong humidity dependency and high price restrict their wide commercialization. In this regards, perovskite type oxides has been the subject of intensive research due to their high thermal stability, low fuel crossover, strong light absorption, high crystalline quality, efficient ion conduction ability and easy fabrication methods (Figure 1).

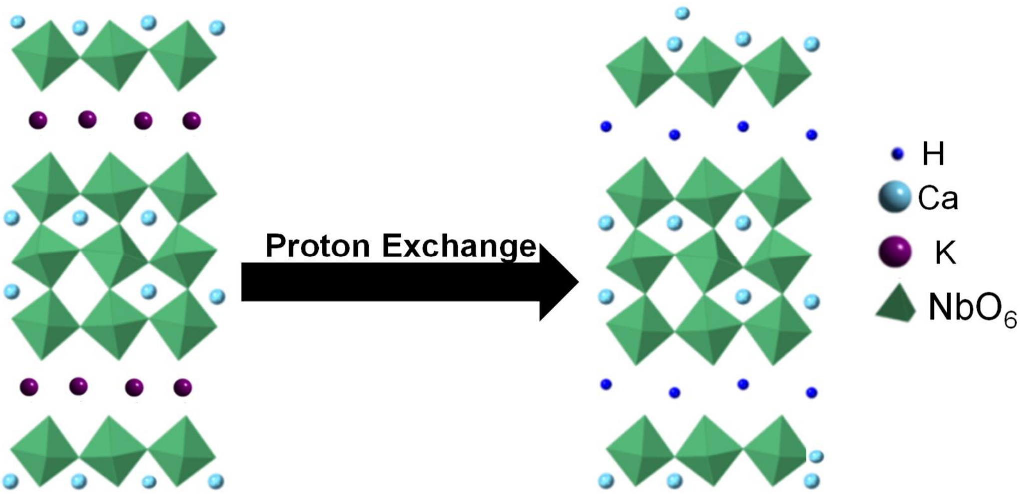


Figure1: Intercalation and ion exchange process in $KCa_2Nb_3O_{10}$

2. Research progress and results in the fiscal year (From October 2023)

(a) Synthesis of Calcium Niobium Oxide Membrane

I have synthesized calcium niobium oxide (CNO) nanosheet by solid state reaction using K_2CO_3, $CaCO_3$ and Nb_2O_5 (ratio= 1.3:2:3) followed by proton exchange and delamination using tetrabutyl ammonium hydroxide (TBAOH). Membrane of these films was fabricated by vacuum filtration and ion exchange using hydrochloric acid. The prepared CNO membrane has good flexibility and mechanical strength to be used as proton exchange membrane in proton exchange membrane fuel cell. The synthesized membrane was characterized using PXRD, XRF, AFM, and SEM to under its structural and morphological characteristics. Analysis of the results (Figure 2) suggests that the formation of CNO was successful. Additionally observation of the cross section

SEM image indicates the layered structure of the CNO film obtained via vacuum filtration.

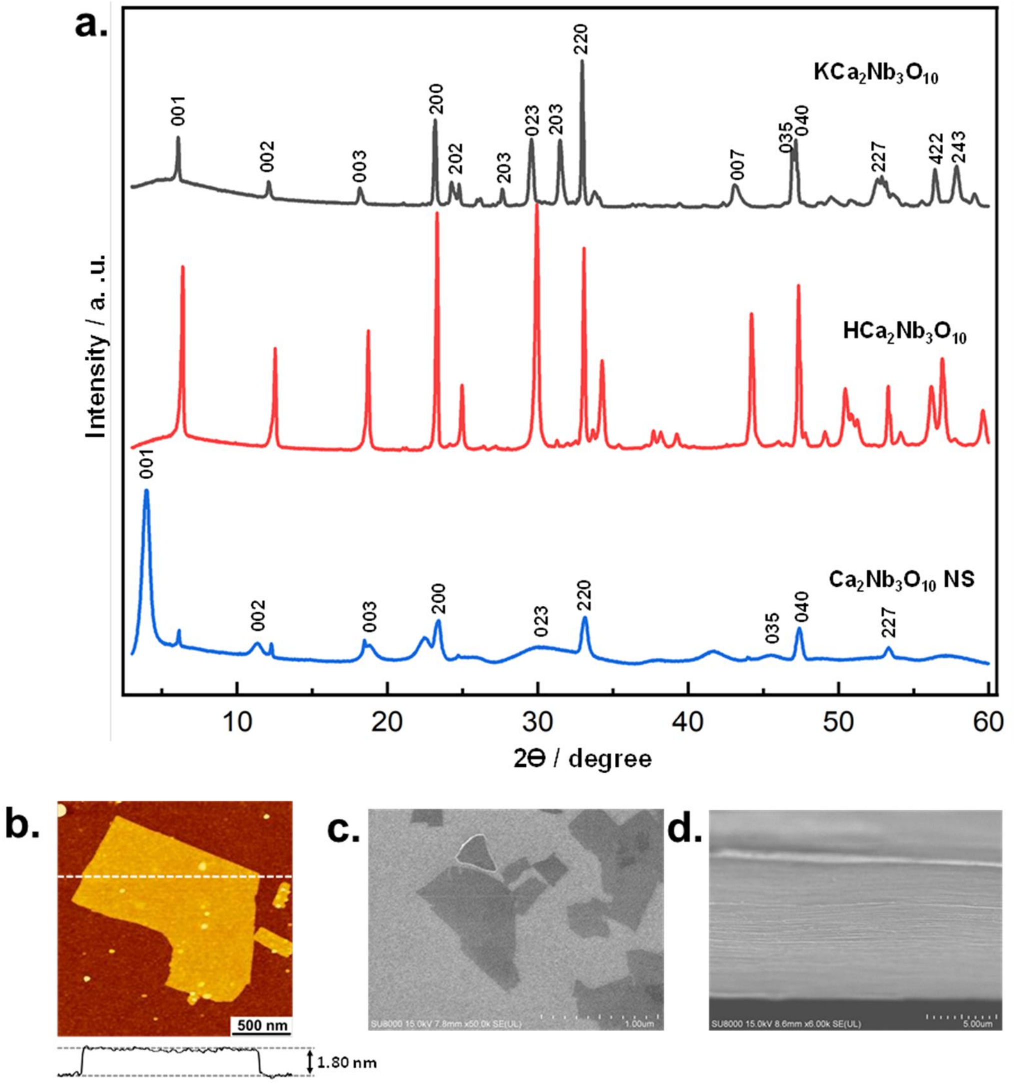


Figure 2: (a) PXRD pattern of $KCa_2Nb_3O_{10}$, $HCa_2Nb_3O_{10}$ and $Ca_2Nb_3O_{10}$, (b) AFM image of CNO, (c) FESEM image of CNO, and (d) Cross section SEM image of CNO.

(b) Application of CNO membrane as solid electrolyte in Proton Exchange Membrane Fuel Cell

Proton conduction ability of the synthesized membrane as proton conductor was evaluated while tuning both humidity and temperature. I have found that CNO give rise to a proton conductivity of 2 $\times 10^{-6}$ S cm^{-1} at 50 ℃ and 40 % RH condition(Figure 3 (a). Under optimized condition, this membrane give rise to a proton conductivity of 4.21 $\times 10^{-5}$ S cm^{-1}. Additionally, study of temperature dependence proton conductivity study showed the usual trend of the increase of proton conductivity with temperature. Calculation of activation energy showed that the proton conduction in CNO proceed via Grotthus mechanism. Finally these membranes were utilized in proton exchange membrane fuel cell using CNO having various thickness and the results obtained shown in Figure 3 (b). When incorporated the CNO membrane having a thickness of 52 μm in proton exchange membrane fuel cell give rise to an optimum power density of 1.17 mW cm^{-2} with optimum current density 2.44 mA cm^{-2}. In comparison to this a membrane with 22 μm showed an optimum power density of 1.95 mW cm^{-2} and current density of 3.98 mA cm^{-2}. These results suggest that CNO membrane can act as `good electrolyte for application in PEMFC with good mechanical strength, proton conductivity and considerable performance in fuel cell.

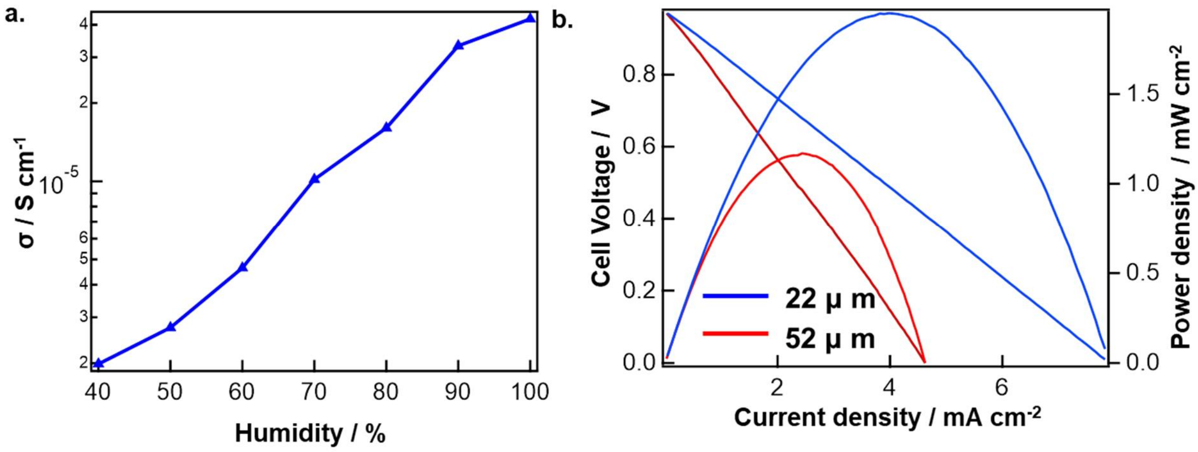


Figure 3: (a) Humidity dependent proton conductivity study of CNO membrane at 50 ℃; (b) Proton exchange membrane fuel cell performance of CNO membrane with different thickness measured at 80 ℃ and 100 % RH condition.

3. Research plan for the next year

The efficiency of a fuel cell is strongly dependent on the thickness of the membrane. However, lower membrane thickness results in poor mechanical strength. Therefore it is necessary to fabricate the membrane using a method that will give rise to a flexible, low thickness and good mechanical strength. Additionally, ion conductivity strongly affected by the length of the ion conduction track. Ion conduction in the traditional metal oxide nanosheet follows long ion conduction track which results in low proton conductivity and lower fuel cell performance. Therefore my future research plan includes the followings:

- ❖ Synthesis of various perovskite type metal oxide nanosheet containing various A-site and B-site cations.
- ❖ Effect of vacancy and dopant on the characteristics of metal oxide nanosheet.
- ❖ Characterization of the as synthesized nanosheet using various characterization techniques.
- ❖ Effect of various fabrication methods on the different properties of the prepared materials for applications in PEMFC.
- ❖ Creating proton conduction nanochannel in various 2D materials such as, metal organic framework, graphitic carbon nitride, layered double hydroxide etc. for application as solid electrolyte in PEMFC.

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

1. Md Mosaraf Hossain, Md. Nurnobi Islam, Shrikant S. Maktedar, Mostafizur Rahaman, **Dr. Mohammad Atiqur Rahman**, Dr. Mohammad A. Hasnat, Ce doped TiO_2 composite for efficient electrocatalytic hydrogen evolution reaction in acidic medium, *ChemAsianJ.*, 2024, e202301143, 1-13.

2. **Mohammad Atiqur Rahman,** Cai Ze, Ryuta Tagawa, Hidaka Yoshiharu, Chiyu Nakano, Md. Saidul Islam, Yoshihiro Sekine, Yuta Nishina, S. Ida, and Shinya Hayami, Engineering Zeolitic Imidazolate Framework Derived Mo-Doped Cobalt Phosphide for Efficient OER Catalysts, Submitted in *ACS Omega*, Current status: Under review.

3. Nonoka Goto,‖ **<u>Mohammad Atiqur Rahman,</u>**‖ Md. Saidul Islam, Ryuta Tagawa, Chiyu Nakano, Muhammad Sohail Ahmed, Yoshihiro Sekine, Yuta Nishina, Shintaro Ida, and Shinya Hayami*, Enhanced OH- Conductivity from 3D Alkaline Graphene Oxide Electrolytes for Anion Exchange Membrane Fuel Cell, Energy Advances, Current status: Under review.

5. **List of awards, grants, and patents**
   N/A

No. 2-3-5	Environmental Applications of Metal Organic Frameworks			
Name	Reeta Rani	Title	Postdoctoral Researcher	
Affiliation	IROAST Email: ranireetu@kumamoto-u.ac.jp			
Research Field	Environment-friendly technology			

[Details of activities]

1. **Research outline and its perspective:**

   At even trace levels, certain ionic solutes pose significant challenges to human health, the environment, and various industrial applications, including semiconductors (Fig. 1). The quantification of ultra-trace ions is frequently carried out using inductively coupled plasma-mass spectrometry (ICP-MS). However, the matrices in which these ions are found can impact the analysis by altering ionization efficiency and inducing space charge effects. As a result, there is a great need for the separation of targeted metal ions from complex matrix samples, such as seawater, commercial chemicals, and wastewater. This demands the development of materials that exhibit exceptional extraction and adsorption capabilities for specific metal ions. Metal organic frameworks (MOFs) are porous crystalline materials made up of organic and inorganic units. Because of high surface area, tunable pore size, ease of functionalization, and high stability, MOFs are widely studied as adsorbents, separation membranes, and functionalized electrodes. MOFs are considered promising materials for environmental remediation applications.

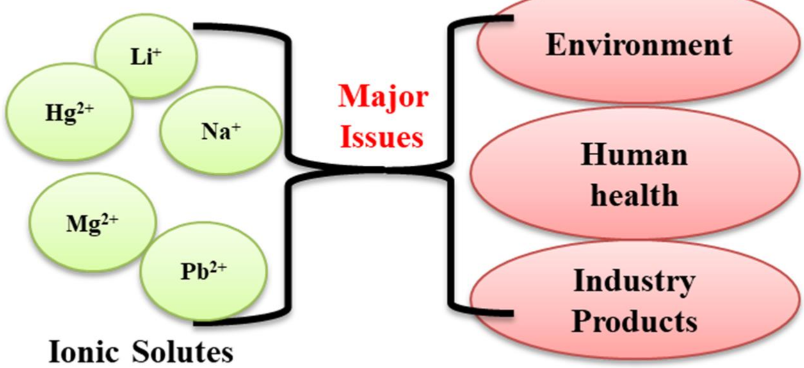


Figure 1: Major issues due to ionic solutes in different matrices

2. **Research progress and results in the fiscal year**

   (a) Utilizing Zirconium based metal organic frameworks for water remediation applications:

   In the first Fiscal year (FY 2022), I synthesized two zirconium metal organic frameworks i.e. UiO-66 and UiO-66-NH_2 (UiO: University of Oslo) using solvothermal method. Zirconium based MOFs have high thermal and chemical stability and adjustable pore size in sub-nanometer range. Therefore, these MOFs are promising candidates for environmental applications like selective separation of ionic solutes. Both MOFs were tested for adsorption of alkali and alkaline earth metal ions. However, none of the two have shown significant adsorption capacity towards tested ions. Further in this fiscal year (FY 2023), a carboxyl group functionalized Zirconium MOF (Zr-MOF, UiO-66-$(COOH)_2$) was synthesized (Fig. 2) and tested for adsorption of alkali and alkaline earth metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+})

from aqueous solutions (Fig. 3).

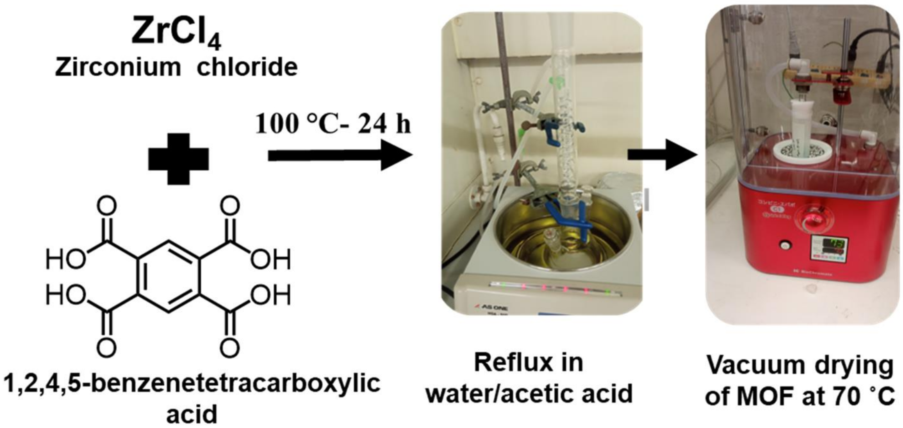


Figure 2: Synthesis and activation of UiO-66-(COOH)$_2$

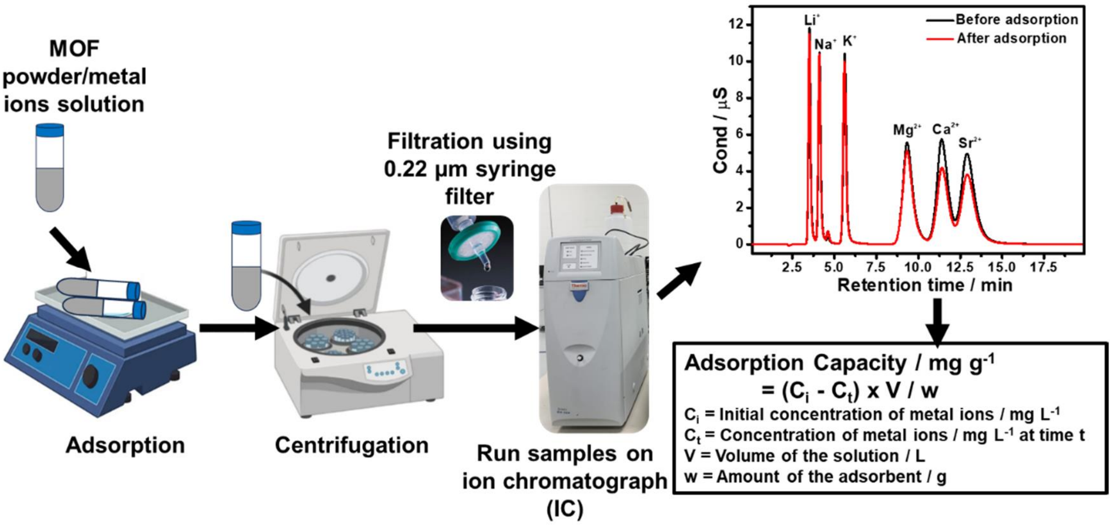


Figure 3: Adsorption study of metal ions on Zr-MOFs

Compared to previously synthesized two MOFs, carboxyl group functionalized Zr-MOF showed significant adsorption capacity for metal ions. Further, the adsorption behavior of Zr-MOF was examined with respect to alkali and alkaline earth metals, considering various solution pH levels, different initial metal ion concentrations, adsorption times, and dosage of MOF. The carboxyl-functionalized Zr-MOF demonstrated superior adsorption capabilities for divalent ions (Sr^{2+} and Ca^{2+}) in comparison to monovalent ions (Li^{+}, Na^{+}, K^{+}) at the natural pH of the solution. This can be attributed to the stronger electrostatic attraction between carboxylic functional group of MOF and divalent ions compared to monovalent ions. The study found that the MOF exhibited optimal adsorption performance with an adsorption duration of 15 minutes, an MOF amount of 0.5 g/L, and an initial metal ion concentration of 0.075 mM at natural pH of the solution as shown in Fig. 4.

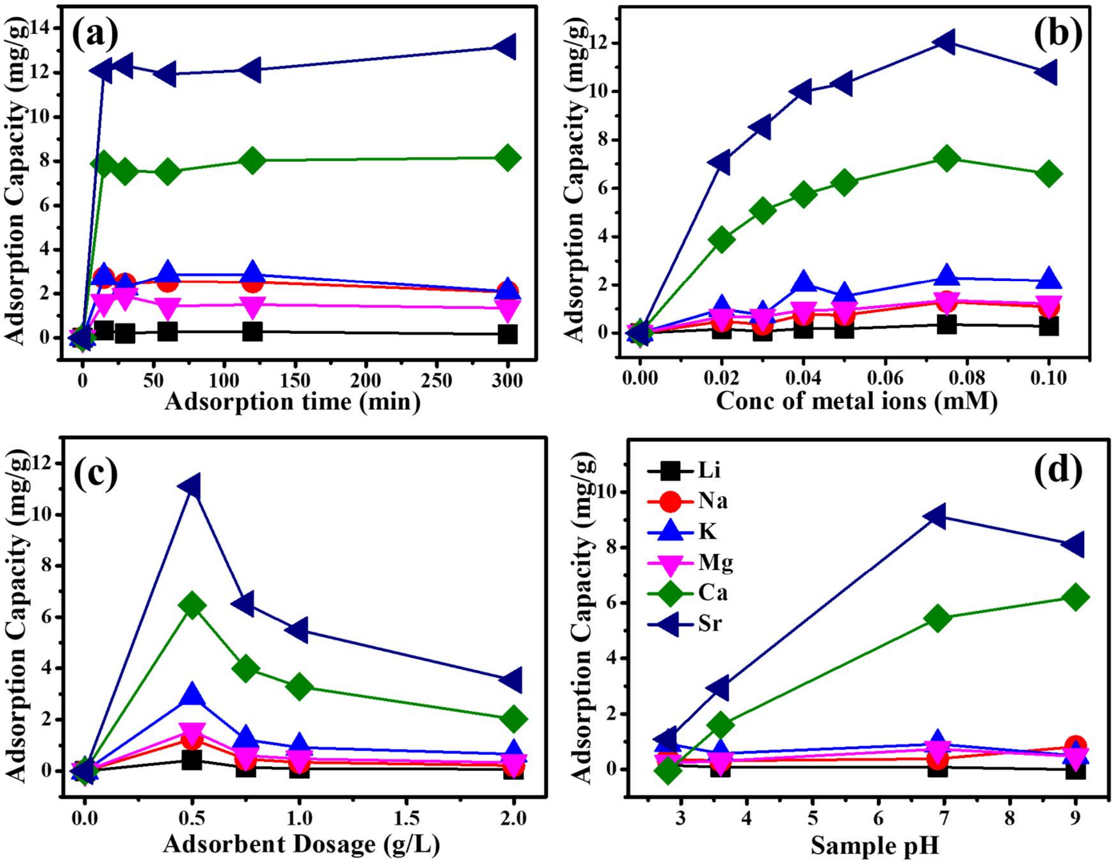


Figure 4: Effect of various parameters, a) Adsorption time, b) Initial concentration of metal ions, c) Adsorbent dosage, d) Sample pH on adsorption capacity of Zr-MOF towards metal ions.

The experimental findings of the present study suggest that carboxyl group functionalized zirconium-based MOFs hold significant potential towards the preparation of suitable sorbents for extraction of metal ions and therefore, in future UiO-66-$(COOH)_2$ modified membranes will be tested for selective transfer/extraction of metal ions from aqueous samples.

3. Research plan for the next year

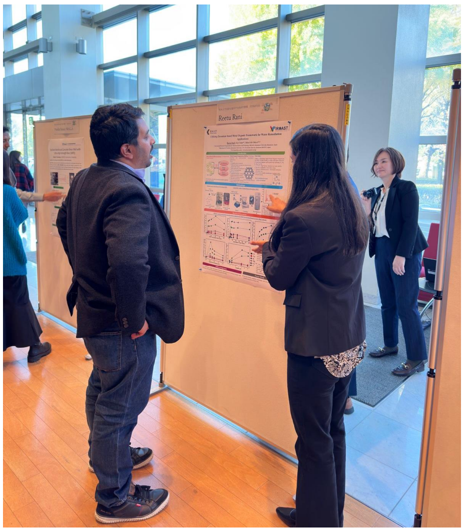
- MOF will be tested for fabrication of membranes for selective transfer of metal ions.
- Real sample studies will be performed.
- Manuscripts will be prepared for submission to reputed international journals.
- Work will be presented at national/international conferences.

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

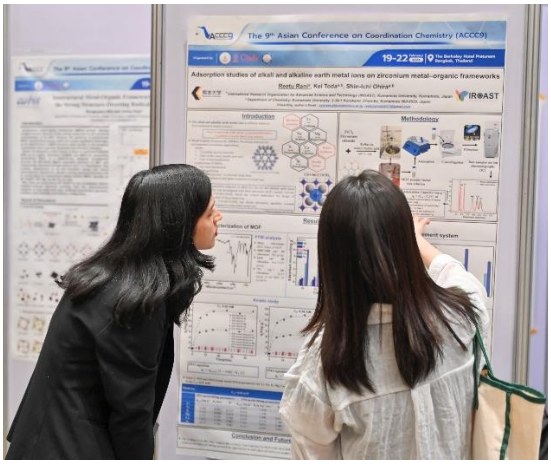
- **Co-authored publication:** M. Garg, **R. Rani,** V.K. Meena, S. Singh, *Significance of 3D printing for a sustainable environment,* Materials Today Sustainability **(I.F. 7.8)**, 23, 1100419 (2023), https://doi.org/10.1016/j.mtsust.2023.100419.

Research Activities:

- Poster presentation: **Reetu Rani**, Kei Toda, Shin Ichi Ohira, *Utilizing Zirconium based Metal Organic Framework for Water Remediation Applications,* in the 18th IROAST Symposium held on 21st NOV, 2023.



- **Poster presentation:** Reetu Rani, Kei Toda, Shin Ichi Ohira, *Adsorption studies of alkali and alkaline earth metal ions on zirconium metal–organic frameworks* at 9th Asian Conference on Coordination Chemistry (ACCC9) in Bangkok, Thailand from 19^{th} -22^{nd} Feb, 2024.



5. List of awards, grants, and patents

- Kumamoto University Financial Support for Female Researchers FY2023 for "Sample matrices isolation for ultra-trace metal analysis in sea water by means of metal organic frameworks-based membranes."
- IROAST International Joint Research Travel Support FY 2023.