ABSTRACT

Fabrication and microscopic characterization of nanosheets exfoliated from artificially-synthesis mica

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Background
The field of two-dimensional (2D) materials with atomic or molecular thickness represent a broad spectrum of materials with exceptional physical and electronic properties, as witnessed by several significant advancements in a short period of time [1,2]. Compared to traditional three-dimensional (3D) bulk semiconductors, the electronic and optical properties of two-dimensional (2D) materials often lead to fascinating phenomena. The phenomena can be attributed to the unique properties possessed by 2D materials, such as the ultralow weight, high Young’s modulus, high strength, outstanding carrier mobility, and strong in-plane anisotropy. Since the successful exfoliation of graphene from graphite, a single atomic layer of carbon has paved the way to study the interesting family of 2D materials. Apart from graphene, significant research efforts have been directed toward 2D semiconducting materials such as boron nitride (h-BN), transition metal dichalcogenides (TMDs), and layered transition metal oxides [3]. By exploiting the unique mechanical and electric properties, 2D materials can be used in wide-ranging applications, including flexible electronics, strain sensors, nano-generators, and innovative nano-electromechanical systems. A layered materials ‘mica’, one of the groups of sheet silicate (phylllosilicate) minerals, is a single-crystalline oxide with a band gap of ~7 eV, has prominent characteristic applications in the electronic and electrical industries because of its optical transparency, uniform high dielectric constant, and mechanical strength as well as its high resistance to heat, water, and chemical agents [4]. Mica is an insulator with an ultra-flat surface and a highly stable structure that can also be used to tune the carrier mobility of other 2D materials, such as graphene, MoS₂, and others [5].

The unique properties of 2D materials greatly depend on the preparation processes. Among them, mechanical exfoliation process is one of the reliable methods to prepare high-quality single crystal 2D materials that can exhibit near-ideal electronic behaviors [6]. Although mechanical exfoliation and transfer techniques help to understand of new physical phenomena, exfoliation techniques fall short in terms of scalability. As for mica, its unique electrical, optical, and mechanical properties of 2D materials considerably depend on the thickness of the mica sheets as well as the interaction with the underlying substrates. With regard to the development of devices using 2D mica nanosheets, having the nanometer-level thicknesses, a conventional and reliable method to prepare high-quality scalable 2D nanosheets and a process that can conveniently evaluate their thickness are of great importance.

Despite the advantageous and unique material properties of mica, fundamental issues with two-dimensional fabrication of mica nanosheets have still remained. Deeper understanding of the mechanism of fabrication of mica at the nanoscale in structural and chemical terms is required for novel functionalization of using mica. One method to finely fabricate the mica utilizes focused
electron beam (FEB) in the processes; a nanofabrication technique with FEB has drawn considerable appeal in terms of the novel capabilities offered [7]. Therefore, it is very important to characterize the mica nanosheets irradiated with FEB and to investigate the mechanism involved with the FEB.

**Aim**

The purpose of this study is to develop a method to prepare large-area and high-quality 2D mica nanosheets as thin as just one layer (1 nm) and to measure their properties as well as the thickness on different substrates such as SiO$_2$/Si wafers, gold- and iridium-coated Si wafers. To mechanically exfoliate the 2D mica nanosheets from bulk mica and affix them on the substrates, we modify the approach by using a polyurethane hand roller. The target mica is artificially synthesis pure mica (phlogopite, KMg$_3$AlSi$_3$O$_{10}$F$_2$). To analyze them, we use scanning Auger electron microscopy/spectroscopy (SAM) as well as atomic force microscopy (AFM), in regard to their 2D shapes and thicknesses with less than 10 layers, and their atomic species. Auger electron spectroscopy (AES) possesses high chemical sensitivity as a surface analytical technique, based on the kinetic energy spectrum of electrons backscattered from the sample irradiated with an accelerated electron beam, which is used to determine the ultra-thin film thickness. The tunneling current and barrier height of few-layer mica are characterized with conductive AFM. In addition, the nanometer-level thickness reduction of mica nanosheets using the FEB is presented and the mechanism for electron beam interactions with mica as an oxide is discussed.

**Results**

We prepared the mica nanosheets with their thickness down to single- and few-layer (one-layer corresponds to 1 nm) on SiO$_2$/Si, Au- and Ir-coated Si substrates using the procedure based on mechanical exfoliation with the polyurethane hand roller. We found that our preparation method reliably yielded single- and few-layer larger-area mica nanosheets, which were evaluated by AFM and SAM. In comparison with other conventional exfoliation methods, our method using the hand roller provided much wider mica nanosheets of a high-quality.

We determined the quantitative thickness of the few-layer mica nanosheets by using AES in regard to the change of peak-to-peak intensities of AES spectra. The Auger spectra showed distinct characteristic shapes and intensities according to the change of the number of layers of mica nanosheets. It has been shown that AES analysis can be used as a standard to determine their thickness in the range of one to six layers of mica film thickness, which has well coincided with the thickness measured by AFM. We derived the inelastic mean free path (IMPF) values for mica nanosheets from the AES peak changes as a function of Auger electron energy which showed good agreement with the universal curve of IMPF, based on plasmon energy loss in solids, for energy dependent electron escape depth. The thickness calibration curves based on the AES peak intensity ratios experimentally obtained for mica nanosheets with different thicknesses. The curves showed the AES intensity attenuation through the mica nanosheets with the IMPF, which is often used in photoelectron spectroscopy. We also observed the SEM images of several-layer mica nanosheets and found that the SEM image contrast changes with increasing number of mica layer. Although SAM analysis of insulating materials tends to be avoided owing to terrible charging effects, we clearly demonstrated that SAM analysis is a powerful method for investigating insulating 2D nanomaterials.

The electronic properties of the mica nanosheets were examined by conductive atomic force microscopy to measure their current–voltage ($I$–$V$) curves, exhibiting the characteristics of metal–insulator–metal contact having a tunneling barrier which was decreased with decreasing thickness.
This shows the fundamental properties of mica nanosheets exhibiting their possibilities toward the novel functional electronic devices. It is likely that this electron tunneling allows us to conduct the SAM analysis by avoiding the terrible charging effect on the insulating mica.

We have performed nanometer-level layer-etching of the mica nanosheets by irradiation with FEB of the SAM setup. The etched regions were in-situ evaluated by AES of the SAM setup, as well as ex-situ AFM. The prolonged FEB irradiation was able to remove the mica elements until the substrate was exposed. The etching rate exponentially increased with irradiation time. The beam energy and current dependence was also examined; the etching rate increased with increasing current but decreasing energy. We discussed the etching mechanism in terms of IMFP of the electrons passing through the mica nanosheets, based on in-situ AES analysis. This study would lead to realization of flexible and transparent electronic devices using fine-patterned mica nanosheets with a desired nanometer thickness.

**Conclusion**

This study proposed a conventional and reliable exfoliation method to be large-area and high-quality mica nanosheets by using the polyurethane hand roller, as well as affixed to the Si substrates with the hand roller. Furthermore, the elemental and structural analysis of even insulating thin 2D mica nanosheets was plainly conducted by the SAM, the information of which is fundamental and critical to realize nanoscale electronic devices. This indicates that SAM analysis is powerful for thin 2D nanosheets, composed of conducting and even insulating. From the AES analysis, the values of IMFP in the mica were evaluated, which are useful for the thickness evaluation of mica nanosheets. The finely-patterned thinning method of the mica nanosheets with FEB was also demonstrated.

For the prospect in the related fields, the advancement of semiconductor technologies has been based on development of integrated circuits that demand the improvements of individual transistor performance in the circuits. Among the different ways of this transistor improvement, the role of the gate dielectric materials is more important to the proper functioning of field effect transistors. Hence, single crystalline materials such as ‘artificially synthesis mica’ is an excellent choice for the gate dielectric material because of its uniform high dielectric constant, high dielectric strength, low power loss, and atomically flat surface free from surface charge traps and surface defects. To use mica as a gate dielectric layer, high-quality nanosheets with precisely designed and measured thicknesses and nanoscale characterization of the mica nanosheets are of great importance. Throughout this research work, to make mica as a proper candidate for novel electronic devices, our developed preparation method and characterization of mica nanosheets using surface sensitive analyzing methods were successfully demonstrated.

**References:**


Research Accomplishment

List of Publication

- Islam Mohammad Razzakul, and Masahiko Tomitori, Evaluation of the discrete thickness of exfoliated artificially synthesized mica nanosheets on silicon substrates: Toward characterization of the tunneling current through the nanosheets, Applied Surface Science (Accepted) (peer review)
- Islam Mohammad Razzakul, and Masahiko Tomitori, Layer-etching of mica nanosheets using focused electron beam, Applied Physics Express (Submitted)

International Conferences

- I.M. Razzakul, M. Tomitori, Evaluation of thickness of exfoliated artificially-synthesized mica nanosheets affixed on silicon substrates and its correlations with Current–Voltage characteristics, 27th International Colloquium on Scanning Probe Microscopy, December 5-7, 2019, Shizuoka, Japan. (Oral presentation) (peer review)
- I.M. Razzakul, M. Tomitori, High-temperature treatments of two-dimensional flakes of phlogopite mica on silicon substrates evaluated by atomic force microscopy, 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures, October 21-25, 2018, Sendai International Center, Sendai, Japan. (Poster presentation) (peer review)

Domestic Conferences and Symposiums

- I.M. Razzakul, M. Tomitori, Evaluation of the thickness of mechanically exfoliated mica nanosheets affixed on Si substrates by scanning Auger electron spectroscopy, 80th JSAP Autumn Meeting, September 17-21, 2019, Hokkaido University, Japan. (Oral presentation)
Mechanics of Wet Adhesion on Patterned Soft Surface, and Application to Development of Soft Robotic Hand

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1. Research Content

The sole toe of the tree frog has a microstructure in the contact interface comprising from a vast number of cells interspaced by a channel system. When contacting with surrounding environments, fluid inside the grooves is ejected to produce the wet adhesion, helping this animal to secure the substrate. Wet interfaces can facilitate the soft robotic fingers to archive an effect grasping thanks to increment of the adhesion interactions with the gripped object. Hence, the wet adhesion mechanism of the tree frog toe hinted us to develop the soft robotic hands for grasping the soft-fragile objects in wet environments. Thus, my thesis illustrates a mechanical approach understand the significant role of morphological design on rising the wet adhesion for secure grasping by the soft pads attached on the robotic finger’s tips. To answer the given question, we firstly constructed a model of contact mechanics for the wet interface between the soft pad and its surrounding substrates. Then, two conditions of these such pads were carried out in comparisons between: a pad with a normal surface (n-pad), and a pad with a micropatterned surface (m-pad). The latter was designed and estimated inspired by the wet adhesion principle between the surface of the tree frog’s sole toes and their environments. In this analytical model, we proposed a method to investigate the contact force for two geometries of the substrates having: flat and curve contact interfaces.

For the flat contact interface, the adhesion and contact forces between the n- and m-pads with their substrate were estimated for both normal and tangential directions. In this scenario, these pads were cast from silicon rubbers. Additionally, a square-patterned mold, as the m-pad mold, comprising from 3600 $85\mu m \times 85\mu m$ cells interspaced by a channel network with $15\mu m$ wide and $15\mu m$ deep was fabricated from the electron beam lithography (EBL) technology. The obtained results of the normal and tangential contact forces for the m-pad and the n-pad were verified through the measurements in wet conditions. Validated results illustrated a good agreement with those of the estimation, revealing that the micropatterned morphology can enhance the contact force for the m-pad by two-fold in case the normal and 1.2- to 1.4-fold in case the tangential force.

The model of contact mechanics with adhesion in flat interface was applied to the flat contact interface. Herein, the adhesion force was focused on the normal direction in different contact scenarios. In addition, the micropatterned pad used in this analysis has 3600 cells each $85 \mu m \times 85 \mu m$ separated by grooves $15\mu m$ wide$\times 44\mu m$ deep. This micropattern soft pad is able to change its
form into a concave or a convex surface. We estimated the normal contact force in detachment and attachment phases between the micropattern soft pad and a substrate (environment). This micropattern pad was compared with a similar pad without a micropattern for their adhesion ability at the interface between the pad and the substrate. Obtained results, have good agreement with the estimations, demonstrated the surface of the micro-patterned pad enhanced contact force at the interface approximately 1±2 times than that the normal surface. This approach can be utilized in evaluation of wet adhesion in grasping curved surfaces of objects using soft pads with patterned surfaces.

Based on the results obtained from the model of the contact mechanics with adhesion, we proposed applications of the soft robotic hands. The first of them is a project of a manipulating robot in automatically attaching and detaching a contact lens from a ‘human eye’. A contact lens presented a hemispherical thin shell was grasped by the soft fingers in three different environments: inside/outside the preservative liquid and as the contact lens stuck a hemispherical substrate mimicking a human eye. The experimental and estimated results were compared for two kinds of the finger’s tips surfaces: normal and micropattern. The tested results illustrated a good contract with the calculation as the m-pad reduced the preload and deformation of the thin hemispherical shell 1.1-2 times lower than that of the n-pad. The next application is a soft robotic hand approaches to grasp and then release a food sample in wet condition. We showcased this scenario with a small block of fresh tofu 19.6mm×19.6mm×15mm which is soft, fragile object that was grasped by a soft robotic hand including two symmetrical pressurized fingers which their tips deposited with two types of soft pads: a n- or m-pads. The micro-machined pattern comprises of 14400 square cells same dimensions as the previous m-pad, whereas each groove has its cross section 15µm in width and 44µm in depth. Our estimation of the grasped force for both types of soft pads were conducted, then verified by actual application in griping the tofu block. Both estimated and experimental results reveal that the micropattern pad decreased the preload and deformation of the tofu block’s surface 2.2 times lower than that of the flat one, for stable grasping of the tofu. The showcase in my thesis confirmed the potential of micro patterns grasping soft-fragile objects in wet environments without complicated control strategy, promising wider applications for robot in medical, human, service or food industry.

2. Research Purpose

Motivation in solving the given problems, our study aimed to develop the novel soft robotic hand enabling grip/manipulation of the soft-fragile objects. In this scenario, the principle and morphological designs of the adhesive pads attached in the robotic fingers are inspired by the wet attachment of the tree frog’s toe pad. Additionally, the role of micro pattern on enhancement of the grasp force/contact force was investigated through constructing theoretical model validated by experimental evidence. Our research makes meaningful contributions to science and tech as followed:

1. Studied the wet attachment mechanism of tree frog’ toe pads for improving the adhesive ability of the pad in robotic finger.
2. Came up with a theoretical model for estimating the wet adhesion force in normal and tangential direction for flat contact interface between the pads (m-and n-pad) and the substrate, which is potential for other related researchers to follow and develop their current works.

3. Developed the approximation of the wet adhesion in flat surface of the pads (m-and n-pad) to two parallel curved contact interfaces between those pads with the curved substrates. Studying curved contact interfaces is more suitable for utilizing the actual applications of soft robotic manipulation because the object’s surfaces may be not completely flat.

4. Presented a theoretical approach for gripping thin hemispherical shell in wet environment by the pad having micropatterned morphology. Our work is useful for evaluating the manipulation of thin soft objects by robotic fingertips with patterned structure in wet or moisture conditions.

5. Showed an analytical model for evaluating the grasping ability of a soft robotic finger’s tip attaching micropatterned pad (m-pad) over a wet, fragile object such as a tofu block. This work is potential for extending to grasping soft-fragile objects in wet conditions by micropattern interface fixed on the fingertips.

6. Demonstrated some ways to making a soft robotic finger’s tips attaching the bioinspired pad with an array of the cells and grooves in microscale.

Keywords: Wet adhesion, dry adhesion, tree frog toe, micropattern, soft grasping and manipulation.

Publications and Awards

Peer-reviewed journals

Other peer-reviewed journals

Peer-reviewed international conference
Peer-reviewed international workshop


Domestic conferences, symposiums


Awards


[3] JAIST Off-campus research grant for research in INRIA Institute, Lille, France, 2019.4-9.

[4] Student travel award by JAIST research grant, 2019.5


High-Throughput Experimentation and Catalyst Informatics for Oxidative Coupling of Methane

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Materials informatics (MI) is one rising area, which applies data-oriented approaches to the research and development of materials science. One of fundamental requirements for MI is the presence of a proper dataset in terms of consistency, distribution, and size. Once such a dataset is prepared, an appropriate learning method is selected from the toolbox. While enormous materials data have been accumulated in literature, they suffer from an insufficient scale, non-uniformity, and anthropogenic biases towards good data with the burial of poor data. Moreover, materials properties such as catalyst performance are highly sensitive to process conditions, while individual research groups have commonly employed their own conditions. In order to overcome the problem of the data scarcity in MI, high-throughput experimentation is considered to be the most promising and effective approach. In this thesis, I attempted to establish complete high-throughput experimentation for the generation of a proper dataset, and implement catalyst informatics to extract knowledge from the obtained dataset. The concept was demonstrated by taking oxidative coupling of methane (OCM) reaction as a case study, which is a long researched reaction toward industrialization.

In Chapter 2, a high-throughput screening instrument was successfully developed for automatic performance evaluation of 20 catalysts at a series of predefined conditions in a fixed-bed configuration. The catalytic test was done in steady states at 900 to 850, 800, 775, 750, and 700 °C. At each temperature, the total flow volume, the CH$_4$/O$_2$ ratio, and the Ar concentration were stepwise varied, leading to 216 conditions per catalysts and 4320 observations for 20 catalysts in a single automated operation. By only 3 operations, 59 catalysts of a Mn-Na$_2$WO$_4$/$\text{SiO}_2$ type were successfully evaluated in OCM, which enabled knowledge extraction using common visualization tools and machine learning techniques. It was found that the OCM reaction is generally sensitive to the process conditions, and catalyst design has a great impact on the process dependence. In particular, the modification of Si-based support affects the performance of Mn-
Na₂WO₄ in terms of the low-temperature activation of CH₄ and the selectivity tolerance against high O₂ concentration.

![Diagram of catalyst informatics](image)

**Figure 1.** Concept of catalyst informatics achieved in this thesis.

In order to explore the origin of the low-temperature CH₄ activation, in **Chapter 3**, a series of catalysts were prepared by depositing the Mn–Na–W active phase on various Si-based supports which differed in the pore size, the structure, and the amount of foreign elements (Al, Ti). The OCM performance of these catalysts was acquired on the developed HTS instrument under various reaction conditions. It was found that high-silica supports were good supports in general, while mesoporous silica supports appeared to be superior at low temperature specifically. From the characterization results, it was elucidated that high-silica supports are advantageous in forming the α-cristobalite phase, which is known to stabilize tetrahedral WO₄²⁻ and Mn₂O₃ active species. The mesoporous silica offered the largest accessible surface area to improve the dispersion of the active phase.

In **Chapter 4**, I aim to discover new catalysts by means of random sampling from a vast materials space, HTS, and data analysis. 300 M₁–M₂–M₃/support catalysts were prepared and evaluated, where M₁, M₂, M₃, and support were randomly selected from a given library. By statistical analysis, I successfully identified individual elements and their binary combinations which are positive for the OCM performance. Machine learning was employed to generalize the effective catalytic system for OCM. The results not only rediscovered known catalysts obtained in
the past three decades, but also newly discovered novel combinations that have never been explored so far.

Based on all of these results, I successfully demonstrated the implementation and power of the MI in the research and development of OCM catalysts, where the presence of high-throughput experimentation was truly indispensable for obtaining a proper dataset.

**Keywords:** High-throughput experimentation, Catalysts informatics, Oxidative coupling of methane, Machine learning, Combination effect
Research Accomplishment

A) PUBLICATION


B) CONFERENCES


2) High-Throughput Experimentation and Catalyst Informatics in Oxidative Coupling of Methane, **Thanh Nhat Nguyen**, Thuy Phuong Nhat Tran, Ashutosh Thakur, Shun Nishimura, Keisuke Takahashi, Toshiaki Taniike, Chemistry Conference for Young Scientists 2020 (CHEMCYS2020), Blankenberge, Belgium, Feb. 19-21, 2020, oral presentation.

2) High-Throughput Experimentation in Oxidative Coupling of Methane, **Thanh Nhat Nguyen**, Thuy Phuong Nhat Tran, Ashutosh Thakur, Shun Nishimura, Keisuke Takahashi, Toshiaki Taniike, The 8th Asia Pacific Congress on Catalysis (APCAT-8), Bangkok, Thailand, Aug. 4-7, 2019, poster presentation.

4) Thermal degradation and stabilization of bio-based polyimide, **Thanh Nhat Nguyen**, Anh Thi Ngoc Dao, Tatsuo Kaneko, Toshiaki Taniike, 10th International Conference of Modification, Degradation and Stabilization of Polymers (MoDeSt 2018), Tokyo, Japan, Sept. 2-6, 2018, poster presentation.

C) AWARDS

Design of High-Throughput Experiments for Three-Way Catalysis

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To meet the increasingly stringent legislation for the gasoline engine exhaust emission, the exhaust aftertreatment systems need a breakthrough in the research and development of three-way catalysts (TWCs). While the catalysis society has made enormous efforts focusing on materials aspects for seeking the best or novel catalyst formulations, the development in methodology aspects, especially high-throughput (HTP) approaches, has just emerged to hold a great promise in that regard. Even though HTP catalyst screening techniques have become a mature and well-established tools in many catalytic systems, their applications in the TWCs have been hardly reported due to both technical and material constraints. The diversity and complexity of the catalytic system and reaction conditions necessitate a primary screening technique to quickly and broadly screen a huge parametric space. This catalytic system also requires highly accurate screening tools to distinguish the activity in a one-digit difference, signifying the essential of implementing secondary screening with higher precision. Therefore, the aim of this thesis is to design an integrated HTP screening protocol for the development of the TWCs.

The upstream of the hierarchical HTP workflow is the primary catalyst screening, which typically requires a fast and non-intrusive technique being capable of truly parallelized screening, preferably based on an optical method. For that, a novel chemiluminescence (CL) method was developed with special emphasis on high-temperature gaseous catalysis. In Chapter 2, the proof of concept of the CL method was formulated by thoroughly studying the CL behavior of the catalytic oxidation of CO and C3H6 by of O2 and/or NO, which are the major processes in a catalytic converter, under both stoichiometric and non-stoichiometric conditions. In this stage, a CL instrument was developed based on the cooperation among a gas mixer, a custom-made CL analyzer using a photonmultiplier as a detector, and an on-line gas chromatography (GC) for simultaneous analysis of the effluent mixture from the CL reactor. The CL activity of these oxidation reactions was confirmed by temperature-ramping measurements, where the CL intensity showed an exponential behavior against the temperature irrespective of catalysts. Steady-state
measurements demonstrated a linear relationship between the CL intensity and reactions rate regardless of stoichiometry, thus the CL intensity is a good measure of the reaction rate. The capability of the CL method in rapid catalyst screening was confirmed by a good linear correspondence between the CL intensity and the catalytic activity in \( \text{C}_3\text{H}_6 \) oxidation by \( \text{O}_2 \) for a series of Rh-based catalysts In Chapter 3, a CL imaging instrument was designed for achieving primary screening of the TWCs. The CL imaging instrument was equipped a reactor cell for gaseous catalysis and electron multiplying charged-coupled device camera for single photon detection in the form of images. The CL imaging technique exhibited the feasibility of a simple, straightforward, and rapid evaluation of catalytic activity based on a good correlation between the CL intensity and the \( \text{C}_3\text{H}_6 \) conversion. In addition, the one-to-one correspondence of the CL intensity obtained from the parallel measurement and their corresponding catalytic activity signified the great potential of the CL imaging technique in HTP catalyst screening. Chapter 4 describes the HTP secondary screening of a simulated lead TWCs library based on a HTP screening instrument featured with fully-automated catalytic evaluation of 20 reactor channels in a wide range of conditions with the aid of a quadruple mass spectrometer. The instrument allowed generation of a large process-relevant dataset at high accuracy, which is satisfactory for the secondary screening. Three-way catalytic reactions were conducted in 49 conditions over 20 catalyst samples, affording 980 data points in one operation. The obtained dataset is of high quality and accuracy, and the catalyst performance (in terms of light-off temperature and width of stoichiometric window) were found consistent with literature data. The reaction conditions cover a wide range of temperature and air/fuel equivalence ratio \( \lambda \), allowing the multi-aspect comparison of the TWCs.

The research conducted in this dissertation would make a considerable contribution on the research and development of automotive exhaust aftertreatment systems in methodological aspects. Furthermore, the developed novel instrument and technique in this research can hold a great promise not only for the automotive catalyst application but also for various analogous catalytic systems.
Figure 1. The developed high-throughput approach for three-way catalyst.

**Keywords:** Three-way catalysts, high-throughput catalyst screening, chemiluminescence imaging, high-throughput screening instruments.
Research Accomplishment

A) PUBLICATIONS


B) CONFERENCES

1. Thuy Phuong Nhat Tran, Ashutosh Thakur, Thanh Nhat Nguyen, Toshiaki Taniike, Operando chemiluminescence method for automotive catalytic converter, The 8th Asia Pacific Congress on Catalysis, Bangkok, Thailand, Aug. 4-7, 2019, poster presentation.


C) AWARDS


ABSTRACT

A Study on the Ordering of the Fe Atoms in Fe₄TiS₂ Structures and Their Magnetic Properties

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1. Research Content

Background

Two dimensional transition metal dichalcogenide (TMDC) structures have received much interest due to the emergence of unique physical or chemical properties by being intercalated with various guest atoms or molecules. Thus, extensive studies have been performed to synthesize such intercalated layered structures for various applications such as superconductors, thermal conductors and magnetic materials [1], [2]. Iron-intercalated titanium disulfide (Fe₄TiS₂) structure, which is one of such materials, had been reported to show various magnetic or thermoelectric properties that varied depending on the concentration of Fe atoms in the van der Waals gaps of the TiS₂ host structure [3]–[5]. So, to fully understand the physical properties of Fe₄TiS₂, it is important to first know the arrangement of Fe atoms.

The structure of Fe₄TiS₂ had been investigated experimentally and theoretically. By applying Rietveld method to X-ray diffraction (XRD) results, Fe₄TiS₂ structures have been reported to have short-range ordering of 2a x 2a x 2c for x = 0.15, superstructures of 2√3a x 2a x 2c (or 2a x 2a x 2c ) for x = 0.25 and √3a x √3a x 2c for x = 0.33 with fractional site occupancies for Fe atoms [6]–[9]. This suggested that the Fe atoms did not maintain perfect superstructure order. These results were reproduced by Monte Carlo simulations of Fe atomic distribution in the van der Waals gaps at concentrations of x = 0.15, 0.25 and 0.33 [10], [11]. The simulations were achieved by assuming repulsive interactions between the Fe atoms within the gaps and the attractive interactions of Fe atoms between neighboring layers. On the other hand, using concentration-wave theory, ten possible ordering such as √3a x a x 2c, 2a x 2a x c, √3a x √3a x c, a x a x 2c, √3a x a x 2c, 2a x 2a x 2c and √3a x √3a x 2c were proposed for Fe₄TiS₂ with Fe concentrations of 1/8, 1/6, 1/4, 1/3 and 1/2 [12]. Even recently, by transmission electron diffraction (TED), Fe₄TiS₂ structures has been reported to show only √3a x √3a superstructure for Fe concentrations of 0.086 ≤ x ≤ 0.703 [13]. So, the arrangement of Fe atoms in Fe₄TiS₂ structures is still a controversy.

Aim

One of the possible reasons as to why these previous reports were inconsistent might be because of the difficulty in making crystals with perfect Fe ordering. XRD only provides average information over a large area of the samples, it might have missed out on some local disordered structures. Thus, it is worth investigating these samples with transmission electron microscopy (TEM) since they could provide more in depth information on the local ordering of Fe atoms in the van der gaps of the host structures. In this study, we have investigated the Fe₄TiS₂ structures with various Fe concentrations systematically to clarify the arrangement of intercalated Fe atoms in the TiS₂ structure by transmission electron diffraction (TED) and scanning transmission electron microscopy (STEM) observation. Especially since atomic resolved STEM image is a powerful tool in identifying individual Fe atoms, it can be used to find the short range ordering of Fe atoms at low intercalation concentrations.
Experimental Results

Fe₄TiS₂ single crystals used in this study were grown using chemical vapor transport (CVT) method with the concentrations of x = 0.05, 0.10, 0.15, 0.20, 0.25 and 0.33. These concentrations were chosen so that a systematic structural analysis could be performed on the samples to clarify the arrangement of Fe atoms. STEM samples were prepared in three different directions of [001] (plan view), [010] and [120] (cross sectional view) directions in order to reconstruct the atomic structures three-dimensionally. STEM observations were performed at thin regions of the [001] samples, containing only three to four layers, so that the contrast of Fe and Ti could be differentiated clearly. This is especially important for x = 0.05, 0.10, 0.15 and 0.20 since the number of Fe atoms were low, a thin region would make it easier to differentiate the Fe and Ti atomic columns. At concentrations x ≤ 0.15, individual Fe atoms from the same plane were identified and showed preferential short-range ordering of √3a. As the concentration was increased to x = 0.20, the number of Fe atoms with 2a ordering increased, as indicated in the STEM image. Its TED pattern also revealed weak 2a × 2a × 2c superstructure reflections, suggesting partial arrangement of 2a × 2a × 2c. At x = 0.25 and 0.33, their TED and STEM results clearly showed 2a × 2a × 2c and √3a × √3a × 2c superstructures, respectively.

Furthermore, TED analysis of these Fe₄TiS₂ single crystals using Patterson method revealed some unprecedented superstructures of √7a × √7a, √31a × √31a and √43a × √43a, which is equivalent to Fe concentrations of 0.14, 0.29 and 0.26, respectively. These superstructures were identified through the inverse Fourier transformation of the superstructure reflections in the TED patterns, which displayed the atomic correlations of Fe atoms. From that, the possible Fe atomic arrangement in the superstructures were then proposed. In these superstructures, the Fe atoms were separated almost equidistant, suggesting that the Fe atoms would always try to distance themselves equally apart and thus, they did not only occupy octahedral sites as previously reported, but at tetrahedral sites as well. The occupancy of Fe atoms at tetrahedral sites was confirmed by STEM imaging which showed some darker contrasts at S site, which is also known as the tetrahedral sites.

So, through the TEM observation and analysis, the proposed factor as to why these Fe atoms arranged in such ways could be the attractive-repulsive interactions of Fe atoms. At low Fe concentrations, since no ordering could be observed along the c-axis in neither the TED nor STEM images, this suggested there was no Fe interaction between the layers and the arrangement of Fe atoms was mainly influenced by Fe interactions within the layers. This idea matched part of the Monte Carlo atomic distribution simulations by Negishi et al. [11], in which their initial calculation considered only the interaction of Fe atoms within the layers and the end results showed a preferential ordering of √3a, regardless of the concentration of Fe atoms. However, when the concentration was increased to x = 0.20, the Fe interactions between neighboring layers affected the arrangement of Fe atoms within the layers as well, and thus created short range ordering of 2a × 2a × 2c for x = 0.20, 2a × 2a × 2c superstructure for x = 0.25 and √3a × √3a × 2c superstructure.

Lastly, the magnetic measurements performed on these Fe₄TiS₂ showed different magnetic orders at different concentrations. Spin glass behavior was displayed at low Fe concentrations at x ≤ 0.20 and ferromagnetic behavior was displayed at higher Fe concentrations of x ≥ 0.20.

To summarize, the new findings in this thesis are as follow. First, the different preferential ordering as concentration was increased. A √3a ordering was preferred at low Fe concentrations, which then switched to 2a ordering at intermediate concentrations and again switched back to √3a ordering at higher Fe concentrations. Secondly, the Fe atoms would distance themselves almost equidistant depending on the Fe concentration. Since the samples were grown at high temperature, the Fe atoms could diffuse along the gap until an equilibrium structure had been formed. So, at low concentrations, most of the Fe atoms did not agglomerate and were scattered. The distance between Fe atoms were determined by interactions of Fe atoms within the gap at low concentrations. At higher concentrations, the interactions of Fe atoms in neighboring layers would affect the distance of Fe atoms in the gap and thus, created ordering in both ab-plane and along the c-axis.
2. Research Purpose

The atomic arrangement of Fe atoms in Fe₇TiS₂ single crystals at different Fe concentrations (x = 0.05, 0.10, 0.15, 0.20, 0.25 and 0.33) were systematically investigated by analyzing STEM images and TED patterns. The observed samples were prepared in three different directions of [001] (plane view), [010] and [120] (cross sectional view) directions in order to reconstruct the atomic structures three-dimensionally. To the best of our knowledge, such systematic structural analysis had never been achieved. At low Fe concentrations, we found that short-range ordering at $\sqrt{3}a$ distance is preferred over $2a$ distance. In addition, we observed short-range ordering of $2a \times 2a \times 2c$ for $x = 0.20$, long-range ordering of $2a \times 2a \times 2c$ and $\sqrt{3}a \times \sqrt{3}a \times 2c$ for $x = 0.25$ and 0.33, respectively. Furthermore, TED analysis using Patterson method also revealed some never been reported superstructures for Fe₇TiS₂ and Fe atoms did not only occupy octahedral sites, they occupied tetrahedral site as well. This proved that TEM is an important technique because of its capabilities in identify the local structures, which could not be achieved using other methods such as XRD.

References:
3. Research Accomplishment

List of Publication
- Yi Ling Chiew, Masanobu Miyata, Mikio Koyano, and Yoshifumi Oshima, Ordering of intercalated Fe atoms in Fe,TiS$_2$ structures clarified using transmission electron microscopy, Journal of Physical Society of Japan 89, 074601 (2020). (peer reviewed)

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- Yi Ling Chiew, Satoshi Abe, Masanobu Miyata, Mikio Koyano and Yoshifumi Oshima, Determination of intercalated Fe atomic arrangement in TiS$_2$ layers using transmission electron diffraction, 66$^{th}$ Japan Society of Applied Physics Spring Meeting 2019, 9 – 12 March 2019, Tokyo. (Oral presentation, peer reviewed)
- Yi Ling Chiew, Satoshi Abe, Masanobu Miyata, Mikio Koyano and Yoshifumi Oshima, A TED study of intercalated Fe atomic arrangement in TiS2 layers, 75th annual meeting of the Japanese Society of microscopy, P-M_47、17th June. 2019, Nagoya Convention center (Poster Presentation, peer reviewed)
ABSTRACT

Design of Thermal Conductive Polymer Nanocomposites Based on Nanoparticle Distribution Control

Doctor of Science (Materials Science)

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Along with the miniaturization and lightweight design of electronic devices, greater demands are constantly raised on materials having high thermal conductivity and low density. Polymer nanocomposites are excellent candidates owing to the general characteristics of polymer materials such as good processability, light weight, high electrical resistivity, and low cost. However, the present polymer nanocomposites usually exhibit insufficient thermal conductivity unless impractical formulations are adopted, and key factors affecting the formation of thermal conductive networks are still unclear. In this thesis, I aimed to study the thermal conductivity of polyolefin/aluminum oxide (Al$_2$O$_3$) nanocomposites to clarify the key factors that affect the thermal conductivity. Polymer nanocomposites with continuous thermal conductive networks were designed based on controlling the selective distribution of Al$_2$O$_3$ nanoparticles. The influences of filler dispersion, filler migration and phase
morphology evolution on the formation of thermal conductive networks were studied, and the relationship of filler distribution and thermal conductivity was investigated. The main research results are as follows:

In **Chapter 2**, I applied a reactor granule technology (RGT) to immiscible polypropylene (PP)/polyolefin elastomer (POE) blends to control the localization of nanoparticles at the interface of PP and POE. The RGT afforded uniform dispersion of in-situ generated Al₂O₃ nanoparticles in PP, and this guaranteed the migration of nanoparticles to the interface of a co-continuous structure when blended with POE. The selective localization of nanoparticles at the interface was never achieved when preformed Al₂O₃ nanoparticles were used, and this fact stresses the importance of uniform dispersion in controlling the migration of nanoparticles.

In **Chapter 3**, the relationship among the filler dispersion, phase morphology evolution and the distribution of fillers was revealed by studying the migration of nanoparticles during the annealing process. It was found that the uniform dispersion of nanoparticles decreased the phase domain size to facilitate the successful migration to the interface. Further, the formation of nanoparticle networks decelerated the phase coarsening during annealing. Contrary, the formation of agglomerates and clusters prevented the successful migration of nanoparticles and thus suppression of the phase coarsening became much less effective.

In **Chapter 4**, a continuous segregated structure was designed to improve the thermal conductivity of PP/Al₂O₃ nanocomposites. I achieved the thermal conductivity of 1.07 W/m K at an Al₂O₃ loading of 27.5 vol%. The same strategy was also used in
combination with RGT to control the balance between the number and density of thermal conductive paths.

In conclusion, the filler dispersion, phase domain size, and filler distribution in nanocomposites have important cooperation to determine the thermal conductivity of nanocomposites (Fig. 1). RGT and other developed strategies are believed to be promising for designing practical thermal conductive polymer nanocomposites.

Fig. 1 Influence of filler dispersion, phase domain size and filler distribution on thermal conductivity.

**Keywords:** Nanocomposites; Thermal conductivity; Network; Immiscible blends; Selective distribution

**Research accomplishment:**

**Publications**


Conferences

1. **Xi Zhang**, Toru Wada, Patchanee Chammingkwan, Toshiaki Taniike, Cooperative Influences of NanoparticleLocalization and Phase Coarsening on Thermal Conductivity of Ternary Nanocomposites, 64th SPSJ Annual Meeting, Fukuoka, Japan, May 27–29, 2020. (Non-peer-reviewed)


3. **Xi Zhang**, Bulbul Maira, Toru Wada, Patchanee Chammingkwan, Toshiaki Taniike, Improved thermal conductivity of PP/POE blends by controlling uniform dispersion and selective distribution of Al_{2}O_{3}, the 12th SPSJ International Polymer Conference (IPC2018), Hiroshima, Japan, Dec. 4–7, 2018. (Non-peer-reviewed)
Dissertation Title: Nanostructured Thermoelectric Materials Fabricated from Chemically Synthesized I-III-IV-VI Quaternary Compound Nanocrystals

Abstract

Thermoelectric (TE) technology has acquired a lot of attention due to the ever-growing demand for energy conversion. The research finding on TE materials is hot topic. However, majority of the high efficiency TE materials contains toxic and rare elements such as Se and Te that are not feasible for real application. To investigate the sustainable TE materials with high efficiency, quaternary copper-metal-tin-sulfide based compounds emerged as promising TE material was selected because it consists of environmental friendly, earth abundant and relatively low-cost elements. This dissertation surrounds on the research work of quaternary copper sulfide-based nanocrystals as building block for TE materials, synthesized by chemical methods. The nanobulk material fabrication approaches, characterizations and TE properties in combination with the methodology to improve the TE figure of merit are all presented in this research work.

Chapter 1 provides the general introduction of the TE materials. This chapter includes the basic concepts of thermoelectrics, conventional TE materials, synthesis, effective methodologies to enhance the thermoelectric efficiency, background about the quaternary copper-sulfide based material and its potential as well as challenges for being selected as TE materials. In this research we decided to counter the high lattice thermal conductivity ($\kappa_{\text{lat}}$) through not only all-scale hierarchical arichitecture but also introducing the copper-aluminium-tin-sulfide based material for the first time in thermoelectrics due to predictions of these system to possess very low $\kappa_{\text{lat}}$. High power factor ($PF$) and low $\kappa_{\text{lat}}$ was not sufficient for Cu$_3$AlSnS$_5$ (CATS) system to acquire high $ZT$ value. The shortcomings of the CATS system were systematically countered with the gradual substitution of Al by Ga, and by introducing nanoincclusions of Cu$_2$SnS$_3$ (CTS). We are the first to investigate the I$_x$II$_y$III$_z$IV$_{5-y}$ (I=Cu; II=Zn; III=Al/Ga; IV=Sn; VI=S; y is to maintain electrical neutrality of the system) based TE materials. Various methodologies available for the nanocrystals synthesis have been discussed and out of all the one pot chemical method was shortlisted for this research due to their unprecedented control on the reaction reproducibility as well as scalability. In other words, this chapter represents the challenges associated with present TE materials have been postulated in combination with a brief outlook about the scope of this research, as one of the plausible solutions.

Chapter 2 describes the synthesis of Cu-Zn-Sn-S nanocrystals using one pot chemical method. After ligand exchange, the nanocrystals were pelletized using pulse electric current sintering (PECS) technique to yield Cu$_3$ZnSnS$_5$ nanobulk material. To lower the $\kappa_{\text{lat}}$, a gradual substitution of Zn with Al was performed in the Cu$_3$ZnSnS$_5$ system to yield Cu$_3$Zn$_{1-x}$Al$_x$SnS$_5$ (x = 0.25, 0.5, 0.75, and 1). Complete substitution of Zn by Al substantially decreased the $\kappa_{\text{lat}}$ and dramatically increased $\sigma$ of the material. $ZT$ value of 0.39 at 658 K was achieved for the Cu$_3$ZnSnS$_5$ material. However, the $ZT$ value could not be significantly enhanced with complete Al substitution, which could be primarily attributed to the $k_{\text{car}}$. These results highlight the production of Cu$_3$Zn$_{1-x}$Al$_x$SnS$_5$ TE materials and unveil the scope for improvement of $ZT$ values by altering transport properties.

The Chapter 3 demonstrate a methodology for curtailing the $k_{\text{car}}$ of the CATS nanobulk TE materials without compromising the already suppressed $\kappa_{\text{lat}}$. This chapter presents the effect of Ga substitution in Cu$_3$Al$_{1-x}$Ga$_x$SnS$_5$ nanobulk materials on the transport properties of the materials has been systematically examined. The $ZT$ value of the
Cu$_3$Al$_{1-x}$Ga$_x$SnS$_3$ nanobulk at $x = 0.5$ was found to be more than twice ($ZT = 0.26$) than the pristine CATS nanobulk at 665 K, primarily because of the significant reduction in $\kappa_{\text{car}}$. Correlation among transport parameters and material structural characteristics of the Cu$_3$Al$_{1-x}$Ga$_x$SnS$_3$ nanobulks ($0.25 \leq x \leq 1$) revealed that a larger fraction of zincblende (ZB) phase leads to a higher $PF$.

The Chapter 4 examines the ability of CTS nanocrystals as nanoinclusions in the CATS system for reducing the $\kappa_{\text{car}}$ without negatively impacting the $k_{\text{lat}}$. The doping content of CTS gradually varied from 0.1 wt%, 1 wt%, 3 wt%, 5 wt% and 10 wt% in CATS. The fabricated nanobulk TE material shows, interestingly, wurtzite (WZ) as a major crystalline phase from 1 wt% CTS content onwards; which increases with the increase in CTS nanoinclusions. A correlation has been observed between the type and content of major crystallographic phase and the thermoelectric performance of the fabricated nanobulk TE materials. Greater content of WZ phase has been associated with the lower $ZT$ value. The results direct the attention towards the role of interface between the nanoinclusion and primary matrix in deciding the fate of, especially, $\sigma$. The 0.1 wt% CTS nanoinclusions leads provided better trade-off between $\sigma$ and $S$ without compromising $\kappa$ and thus improved the $ZT$ value 3x than neat CATS system. The 0.1 wt% CTS containing sample possess greater ZB phase content than any other pellets under consideration and prevail the importance of symmetric crystal structure content in deciding the fate of TE properties.

Chapter 5 disseminates the general summary and conclusions followed by the future prospects of the research presented in this dissertation. The results highlight the importance of co-ordination between the material crystalline structural traits and $ZT$ value of I$_3$-III-IV-VI$_5$ based TE materials without using rare and/or highly toxic elements. This research provides an important insight in understanding the behavior of ZB-/WZ-rich nanobulk TE materials. The correlation observed among material structural traits that apart from nanostructuring, the greater content of more-ordered crystalline phase plays an important in regulating the transport characteristics. On the other hand, the mechanistic details for understanding the reasons which affects inherently the content and the distribution of ZB/WZ phase fraction in the material in association with their respective electrical and thermal transport properties represents a challenging yet interesting future outlook.

**Keywords:** Thermoelectrics, Quaternary Copper Sulfides, Crystallographic Phases, One Pot Chemical Synthesis, Nanocrystals

**List of Achievements**

**Published Journal Articles**


Conference Presentations


Development of TiO₂/graphene nanocomposites as visible-light active photocatalysts for water treatment

Doctor of Philosophy (Materials Science)

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Research Content

Heterogeneous photocatalysis using titanium dioxide is a well-known advanced oxidation process for water treatment. However, the large band gap, a short lifetime of photo-excited electron-hole pairs, and the ability as an absorbent limit its applications. Hybridization of TiO₂ with graphene emerges as a promising approach to diminish these drawbacks. Many efforts have been reported on the preparation of TiO₂/graphene composites, but most of them utilized graphene oxide (GO) as a starting material. Subsequent reduction of GO into so-called reduced graphene oxide (rGO) leads to the formation of defect-rich graphene with disadvantageous electronic properties. Furthermore, the aggregation of TiO₂ is usually observed because the sensitivity of titanium alkoxide to water (GO usually contains) significantly impedes the uniform and controlled growth of TiO₂ on graphene. Hence, the aim of this thesis is to explore a novel and effective approach for the preparation of the TiO₂/graphene nanocomposites to obtain excellent visible-light photocatalysts for water treatment application.

In Chapter 2, a novel GO-free route for the fabrication of TiO₂/graphene nanocomposites was explored. This route involved the ultrasonication-assisted exfoliation of graphite in a titanium tetra-n-butoxide and subsequent sol-gel reaction to form TiO₂ using the graphene dispersion. Featured with various advantageous characteristics including i) a morphology in which TiO₂ nanolayers uniformly and thinly covered graphene sheets, ii) a trace amount of
defects on the graphene frameworks, iii) a dramatic inhibition of charge carriers recombination, and iv) a significant extension of absorption edge into visible-light area, the obtained the TiO$_2$/graphene nanocomposites exhibited an excellent performance for the visible-light photocatalytic decomposition of methylene blue in an aqueous medium.

Chapter 3 concentrated on the exploration of new solvents for liquid-phase exfoliation of graphite via ultrasonication. Various new exfoliating solvents were found through screening of different solvents and their mixtures. Particularly, chlorobenzylamine, which is a combination of the molecular structure of chlorobenzene and benzylamine, known as famous exfoliating solvents, presented the highest graphene yield. More importantly, a synergistic effect among different functional groups e.g. aromatic, amine, and halogen groups was identified, and this was more effectively exploited in a form of solvent mixtures. In addition, the preparation of a graphene dispersion in the presence of different metal alkoxides was demonstrated, which could be useful as a direct precursor of various oxide@graphene nanocomposites without mediating GO.

In Chapter 4, further improvement in the visible-light photocatalytic performance of the TiO$_2$/graphene nanocomposites was achieved by chlorine doping. The chlorine-doped TiO$_2$/graphene nanocomposites were synthesized based on the synthetic method established in Chapter 2. With the aid of chlorine radicals in accelerating the photodecomposition of target organic compounds and a significant reduction of the amount of graphene defects, the chlorine-doped TiO$_2$/graphene nanocomposites exhibited a significant improvement in the photocatalytic performance compared to that of the undoped TiO$_2$/graphene nanocomposite (Figure 1).
Research Purpose

Because of the limitations of the conventional TiO$_2$/rGO nanocomposites which restrained their photocatalytic activity, in this research, I have found a novel GO-free route to synthesize TiO$_2$/graphene nanocomposites. Eliminating most of the problems of TiO$_2$/rGO, I have synthesized the TiO$_2$/graphene nanocomposites with an excellent visible-light photocatalytic activity.

Owing to my finding about the importance of solvents in the preparation of the nanocomposites, in which their ability to stabilize graphene played a key role, I have investigated deeper about the solvents for the liquid-phase exfoliation of graphite under ultrasonication. In this research, I have explored a series of new exfoliating solvents. More importantly, the relation between functional groups of solvents and their exfoliation ability has been found. A synergy between effective functional groups introduced not only in the molecular structure of single solvents but also more exploited through solvent mixtures. This finding is meaningful for chemists in investigating a proper exfoliation medium for specific purposes in term of the availability, diversity, and tunability.

According to the finding of the synthetic method for TiO$_2$/graphene nanocomposites as well as the available solvents for the preparation of the nanocomposite. With the ambitious to further improve the photocatalytic activity of the TiO$_2$/graphene nanocomposites by chlorine doping, I have investigated a novel synthetic method for Cl-doped TiO$_2$/graphene
nanocomposite. The Cl-doped TiO$_2$/graphene nanocomposites successfully prepared by this new method exhibited an excellent enhancement in the visible-light photocatalytic activity compared to the undoped ones.

In general, this thesis has established a novel and effective route for the synthesis of the TiO$_2$/graphene nanocomposites and demonstrated its usefulness in the field of water treatment based on excellent visible-light photocatalysis. It was also suggested that a similar method is applicable for the synthesis of different oxide@graphene nanocomposites with advantageous features.

**Research Accomplishment**

A) Publications


B) Conferences


Studies on Organic/inorganic Composites of Bio-based Polyamide Derivatives from 4-aminocinnamic Acid

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Part 1: Research Content

Background: The overdependence on petroleum-based plastics (polyester, polyethylene, polypropylene, and polystyrene) has been contributing to natural resource depletion, waste accumulation, and global warming. Consequently, the use of bio-based polymers, which are derived from renewable materials is essential as a part of solving the plastic problem. However, the bio-based polymers still exhibited low performance for super-engineering plastics and their associated applications. Bio-based polymers possessing considerable performance similar to that of conventional super-engineering plastics are desired. This provides several advantages like polymer recyclability, CO₂ stocking, and contribution to the deceleration of global warming.

The organic/inorganic composites are considered as functional polymers. The functional polymers are the class of polymer (with heterogeneous backbone chain) possessing available reactive and polarizing functional groups. With these functional groups, the polymers often offer new or enhanced properties. The addition of inorganic materials has been proven to provide the polymer with novel or improved properties. This could be done through techniques such as halogenation of polymer side chain, quaternization, metal-complex formation and direct mixing.

The exotic 4-aminocinnamic acid (4ACA) was previously created from the fermentation of sugar by Escherichia coli. Through 254 nm UV irradiation of 4ACA, [2+2] photocycloaddition occurred, and a bio-based aromatic diamine, 4,4’-diaminotruxillic acid (4ATA) was produced. 4ATA became the monomer that led to the creations of high-performance bio-based polymers such as biopolyimide (BPI) and biopolyamide (BPA). Taking into account the structure of 4ATA the organic/inorganic composites can be developed from the monomer according to the desired functions. The benzenes provided the structure with performances related to thermal and mechanical properties. The cyclobutane was responsible for the rigidity. The carboxylic acid (COOH) offered an anionic property, while the ammonium (N₂H) is cationic in nature. The applications of interest include anion scavenging, flame retardancy, and photoluminescent.

Aim: In this thesis, we would like to develop high-performance functional materials from renewable sources for a sustainable society. The main aim is about modifying 4ACA and its bio-based polymers derivatives to create organic/inorganic composites for desired functions. This takes into account the available functional groups on the existing BPA and BPI side chains, mainly COOH and NH groups. We expect that by making organic/inorganic polymer composite, novel properties of the polymer will be created. This would expand the bio-based polymer applications such as anion scavenging, flame retardancy, and photoluminescence.

Experimental: A multifunctional monomer, 4,4’-di(trimethylamino)-α-truxillic acid (Q-4ATA) was synthesized by the quaternarization of 4ACA and polymerized with various diamines to obtain a series of cationic BPA. The structure of Q-4ATA was confirmed by NMR and mass spectrometry. The cationic BPA was characterized by the thermogravimetric analysis (TGA), gel permeation chromatography, Fourier-transform infrared spectroscopy, solubility tests, and a sustainability metric (percent use of renewable resources calculation). One application of the cationic BPA bearing quaternary ammonium was the anion-exchange ability. Consequently, they were employed to remove
iodide (I⁻) from the water for the radioactive iodine remediation application. The removal of I⁻ was examined by kinetic and batch experiments at various conditions including cationic BPA dose, time, I⁻ concentration, pH, presence of competitive anion, regeneration cycles, and temperature.

The BPI in the form that contained carboxylic acid (BPI-COOH) was modified by neutralization with KOH to form a potassium salt, BPI-COOK. Complexation by an exchange of K⁺ into targeted multivalent metal ions (Al³⁺ and Cu²⁺) was performed. BPI-COOAl and BPI-COOCu films were obtained. The thermodynamic was determined by performing complexation at various metal ion concentrations and temperature. The composites were studied for its flame retardant properties by the Underwriters Laboratories standard 94 for vertical burning test (UL-94V) and microscale combustion calorimetry (MCC) analysis. The mechanism of flame retardancy was investigated by analyses of char formations using the Raman spectroscopy, scanning electron microscope, and X-ray photoelectron spectroscopy flame retardant mechanism. In addition, thermo-mechanical properties (TGA and tensile measurement) and optical transparency (Ultraviolet–visible spectroscopy) were determined.

**Part 2: Research Purpose**

**Results and Discussion:** The cationic monomer, Q-4ATA, was successfully obtained (Figure 1a). ¹H and ¹³C NMR exhibited signals for all Q-4ATA hydrogen and carbon, respectively. The mass spectroscopy spectrogram of Q-4ATA depicted an adjusted peak of M⁺ that is equal to 206.11735, which was found to be similar to the calculated m/z of 206.11756. The cationic BPA (PA-R1, PA-R2, PA-R3, and PA-R4) were synthesized (Figure 1b). All kinds of cationic BPA were soluble in aprotic solvents and possess high thermal properties, with 10% weight loss temperatures (TD10) of 296–329 ºC. The BPA consisted of more than 50% renewable source (sustainability metric) in its structure with PA-R4 having more than 95%. The I⁻ removal of PA-R4, from the experiment, q, and the Langmuir equation fitting, qmax, were calculated to be the maximum of the series at 30.0 and 32.3 mg/g, respectively. The high solubility of the BPA in aprotic solvents provides for easy processing. With 120 min equilibrium time, more than 80% adsorption of 10 mg/L initial I⁻ concentration in 90 °C was confirmed. The reusable PA-R4 is not only considered to be fully bio-based, but its anion-exchange processes in the water were observed to be stable throughout different temperatures and pH. It also has a fair selectivity toward I⁻ and is reusable after KOH regeneration.

Complexation by an exchange of K⁺ into Al³⁺ and Cu²⁺ was determined to be an exothermic reaction. When compared to the values of the polymer films in the literature, BPI-COOAl (Figure 2a) and BPI-COOCu (Figure 2b) were suitable as flame retardant materials. Both films were rated V-0 for the UL-
94V test. The THR value (4.5 W/g) of BPI-COOAl was lower than those of BPI-COOH, BPI-COOK, or other polymer films reported in the literature. BPI-COOAl had a $T_{d10}$ of 431 °C and a tensile strength of 64 MPa, exhibiting an improvement of thermo-mechanical properties by metal substitution, as compared to BPI-COOK. The $T_{fs}$ transparency value (83%) of BPI-COOAl was preserved after the metal substitution. The Cu$_2$O and Al$_2$O$_3$ char layer, formed during the material degradation, functioned as an intumescent material to suppress the transfer of heat and promoted flame retardancy. Further study should consider the minimization of metal concentration and incorporation of environmental-friendly additives into the molecular design to create a high-performance film. In addition, the metal-scavenging BPI could also be employed for removing toxic metal ions from a water environment.

Figure 2. Structures and images of flame retardant films created by the complexation of BPI-COOK film submerged in metal ion solution. (a) BPI-COOAl, (b) BPI-COOCu

BPI complexes containing the carboxylate lanthanide (BPI-COOEu and BPI-COOTTb) were produced with lanthanide ions (Figure 3). Under 330 nm, BPI-COOK and BPI-COOH (as controls) developed emission at around 370 – 460 nm. This band was carried over to the emissions of complexes. BPI-COOEu yielded emission bands at 579, 592, 616, 650, and 692 nm which were associated with the $^5D_0 \rightarrow ^7F_J$ ($J = 0 – 4$) transition of Eu$^{3+}$. The prominent band at 616 nm resulted in red emission that could be observed by naked eyes. For BPI-COOTTb, the main emission bands at 489, 545, 587, and 621 nm were ascribed to the transition $^5D_4 \rightarrow ^7F_J$ ($J = 3 – 6$). Due to the overlapping between some BPI-COOTTb emission bands (489 and 545 nm) and the emission at 370 – 460 nm, blue-green emission was observed by naked eyes. The VOCs sensor application was tested for BPI-COOEu. The methanol and ethanol caused enhancement effects on the emissions. The quenched emission by acetone could be explained by the solvent having the region of UV adsorption range (300 – 360 nm) similar to BPI-COOEu. Another mechanism involved lone pair-$\pi$ interaction between a lone pair from the O atom ($sp^2$ orbital) of acetone and a $\pi$ bond of an aromatic ring in BPI-COOEu. The adsorption of UV and transfer of energy by an aromatic ring in BPI-COOEu was dependent on the excitation (HUMO $\rightarrow$ LUMO) of $\pi$ bonds. The lone pair-$\pi$ interaction may prevent the excitation and result in the quenching effect.

Figure 3. Structures and images of photoluminescent films viewed under xenon lamp at 330 nm. (a) BPI-COOEu, (b) BPI-COOTTb

Conclusion: The organic/inorganic composites of BPA and BPI were synthesized by the 4-aminocinnamic acid (4ACA). These polymers bearing novel functional groups and structures were tested for their performances according to the desired applications. Q-4ATA was developed to contain quaternary amines. The monomer was polymerized with diamines into several cationic BPA, which were characterized and used for I$^-$ removal. BPI-COOH was modified in KOH to obtain a polymer containing carboxylate-potassium salt (BPI-COOK). BPI-COOAl, BPI-COOCu, BPI-COOEu and BPI-COOTTb salts were obtained from a simple complexation process where BPI-COOK films were left in
contact with the metal ion solutions. The exchange of K⁺ into the targeted multivalent metal ions such as Al³⁺, Cu²⁺, Eu³⁺ and Tb³⁺ on the carboxylate side change was determined to be an exothermic reaction. With the formation of metal carboxylate complexes, BPI-COOAl and BPI-COOCu became flame retardant. Both complexes exhibited an improved thermo-mechanical property, and BPI-COOAl retained its optical transparency when compared to those of its precursors. With an addition of a rare earth metal, the BPI-COOEu and BPI-COOTb displayed photoluminescent property. BPI-COOEu displayed enhanced and quenched emissions due to solvent contact. This served as the underly mechanism of the material to be developed into the VOCs sensor. The developments of bio-based organic/inorganic composites of BPI and BPA depicted creative and practical ways of producing efficient bio-based functional materials in green society.


Keywords: Polyamide; Polyimide; Ion-exchange; Flame Retardancy; Photoluminescent

**Part 3: Research Accomplishment**


**Conferences:**

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Poly(ionic liquid) Based Binders for Highly Durable Li-ion Secondary Batteries.

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Keywords: Poly(ionic liquid)s, lithium-ion batteries, graphite anodes, binders, interfacial tuning, surface-functionalized silicon nanoparticles, structure-activity relationship.

Research Content

The current thesis is based on the design and development of poly(ionic liquid) (PIL) based materials for Li-ion secondary battery (LiB) applications. Most of the commercial LiBs have graphite-based anodes. The performance and safety of these LiBs depend predominantly on the electrode-electrolyte interface, generally referred to as the solid electrolyte interface (SEI). Hence, it is very crucial to tune the SEI both compositionally and morphologically to enhance the performance of LiBs. PILs is a class of innovative polymers which combines the properties of ionic liquids such as ionic conductivity, electrochemical and chemical stability and non-flammability with the mechanical toughness and processability of polymers. Ohno et al. have explored the use of PILs as in the energy application as electrolytes and have derived very promising results. Yuan et al. have reported the ability of the PIL to enhance the charge carrier ability at the electrode-electrolyte interface by creating a PIL/electrolyte heterojunction. This ability of PILs can be exploited to enhance the interfacial properties of the electrodes. The availability of a plethora of structurally diverse PILs allows for interfacial tuning to obtain the desired properties. This thesis explores the interfacial tuning using PIL based binders and surface modification of the active material by PILs as shown in Figure 1. The relation of PIL structure vis-à-vis its performance has been investigated to understand the role of the substituent and the counter-ion.

Chapter 2: Allylimidazolium Based Poly(ionic liquid) Anodic Binder for Lithium-ion Batteries with Enhanced Cyclability.

In this chapter, the design and synthesis of an allylimidazolium based PIL as a binder for graphite anode were carried out. Engineering the structure and HOMO-LUMO levels of the binder is very crucial in tuning its properties. Though the binder constitutes a very small fraction of the gravimetric weight of the electrode, it can have a great effect on the performance of the LiB. Poly(vinylbenzylallylimidazolium bis(trifluoromethane)sulfonylimide) (PVBCAlmTFSI) comprising an imidazole heterocycle and allyl substituent (Figure 2) was used as a binder.
for graphite anodes in lithium-ion batteries. DFT based theoretical studies also speculated the suppression in the electrolyte degradation in the case of PVBCAIImTFSI binder due to the positioning of its HOMO-LUMO levels as compared to the electrolyte. As predicted, anodes with the PVBCAIImTFSI binder exhibited lesser electrolyte degradation, decrease in intercalation-deintercalation, over potential and higher lithium-ion diffusion. Electrochemical Impedance Spectroscopy (EIS) results showed decreased interfacial and diffusion resistance for PVBCAIImTFSI based electrodes after cycling. Dynamic Electrochemical Impedance Spectroscopy (DEIS) results indicated that the SEI resistance for the PVBCAIImTFSI based anodes to be three times lesser than the PVDF based anodes. A reversible discharge capacity of 210 mAh/g was obtained for PVBCAIImTFSI based half-cells at 1C rate as compared to the 140 mAh/g obtained for PVDF based anodic half-cells. After 500 cycles, 95% retention in the discharge capacity was observed. Also, PVBCAIImTFSI based anodes exhibited better charge-discharge stability than the PVDF based anodes. Suppression of electrolyte degradation, reduction in the interfacial resistance, enhanced wettability and optimal SEI layer formed in the case of PVBCAIImTFSI based anodes cumulatively led to enhanced stability and cyclability during the charge-discharge studies as compared to the commercially employed PVDF based anodes. Thus, the tuning of the interfacial properties leads to the improvement in the performance of the lithium-ion batteries with PVBCAIImTFSI as a binder. A graphical representation of the functioning of the binder is shown in Figure 3. However, it is crucial to understand the effect of the substituent and the counter-ion on the PIL vis-à-vis its performance as a binder. This is investigated in the next chapter by evaluating the performance of the PILs with different substituent and counter-ion.

**Chapter 3: Effect of the PIL Binder Structure on the Performance of the Lithium-ion Batteries.**

Two structurally varying poly(ionic liquid)s were synthesized to understand the effect of the PIL structure on its performance as a binder in LiBs. This will help in the tuning of the polymer structure to optimize its performance in LiBs. The properties of ionic liquids such as ion conductivity, glass transition temperature, viscosity etc. can be tuned by a simple modification of the side-chain or changing the counter-ion. Side-chains such as allyl group increases the ionic conductivity and decreases the viscosity of the ionic liquids. Counter-ions especially FSI assists in the formation of a better electrode-electrolyte interface. Therefore, in this study, the design of PILs was carried such that one of the PILs PVBCAIImFSI contain both the allyl side-chain and FSI anion. The other PIL PVBCBImTFSI has an alkyl chain and TFSI anion. Cyclic voltammetry studies indicated a suppressed electrolyte degradation for PVBCAIImFSI based anodes leading to the formation of a better interface. This was supported by the DEIS measurements whose results indicated lesser $R_{SEI}$ values for the PVBCAIImFSI based anodes. Also, the lithium-ion
diffusion kinetics was found to be better in these electrodes. The charge-discharge measurements were carried out to evaluate the durability and stability of the electrodes. Half-cells with PVBCAlmFSI based graphite anodes showed enhanced durability up to 1500 cycles with a 60% capacity retention. By changing the TFSI anion to FSI in PVBCAlmTFSI, a 400% increase in capacity retention was observed after 1500 cycles. Whereas PVBCBImTFSI based LiBs showed lower capacities with lesser durability. The current study highlights the importance of the side-chain and the counter-ion present on the PIL vis-à-vis its performance as a binder in LiBs as shown in Figure 4.

Chapter 4: Surface Tethered Poly(ionic liquid) for Silicon Nanoparticles in Li-ion Battery Composite Anodes.

The above results show the ability of the PILs to tune the electrode-electrolyte interfacial properties. This led us further to design surface-modified silicon nanoparticles for composite anodes to obtain higher capacities than the conventional graphite anodes. In this chapter, poly(ionic liquid) (PIL) tethered silicon nanoparticles were investigated (Figure 5) as active material in combination with graphite for lithium-ion battery composite anodes. The results obtained are encouraging and calls for more optimization of functionalization and PIL structure. Silicon falls into the category of high energy density materials with a gravimetric energy density of over 4000 mAh/g, has immense potential to plug the current energy demand. However, due to the inherent volumetric changes researchers have failed in many attempts to commercialize silicon anode based lithium-ion batteries. Formation of a passivation layer (SEI) at the electrode-electrolyte interface is very crucial in preventing the damage to the electrode in the harsh cycling conditions. An ideal SEI layer must be ionically conductive and electronically non-conducting. The PILs are known to possess good ionic conductivity and can act as interface enhancing agents to design a better interface. In this work, PIL functionalized silicon nanoparticles were prepared by esterification of poly[1-(5-carboxypentyl)-3-vinyl-1H-imidazol-3-ium bromide] with hydroxyl functionalized silicon nanoparticles. Cyclic voltammetry studies of PIL functionalized silicon nanoparticles based composite anodes indicated an increase in the lithiation-delithiation currents with the cycling. They also exhibited a very high lithium-ion diffusion coefficient of about $1.01 \times 10^{-8}$ cm/s which indicated a robust and conducive SEI formation. These electrodes exhibited about 735 mAh/g of reversible discharge capacity after 34 cycles. This chapter presents preliminary results and performance of the anodes can be improved by more fine-tuning of the PIL structure and functionalization.

Research Purpose

The purpose of this thesis is to design and develop PIL binders for LiB anodes. LiBs have been the backbone of many technological advancements in the last couple of the decades. Due to their high energy density, lightweight, design flexibility and better life-span compared to the other battery technologies, it has been the choice for powering most of the devices. However, the performance of LiBs is strongly affected by the electrode-electrolyte interfaces. Generally, this interface is referred to as the solid electrolyte interface (SEI) results due to the electrolyte degradation on the surface of the electrode. Though being very crucial, the understanding of the SEI is vague and not very well established. On one hand, a thick and dense SEI can limit the electron tunnelling preventing the further degradation...
of the electrolyte. On the other, SEI formation and further growth lead to irreversible electrolyte and lithium consumption leading to high irreversible capacity, capacity fade, increased cell resistance and lower power densities. Therefore to improve the cyclability and the performance of LiBs it is very important to tune the properties of the SEI. Among many approaches to design the SEI, use of a functional binder has been one of the most successful ones. The conventional role of the binder is to bind the active material and other electrode components to the current collector. However, by rational structural design and incorporating certain functionalities into the binder structure, the ability to assist in the interface formation can be achieved. Poly(ionic liquids) or PILs contain ionic liquid moieties covalently integrated into the polymeric chain. The physicochemical properties of this class of materials similar to ionic liquids depend strongly on the PIL structure.

The originality of the work lies in the design of the PIL structure based on the theoretical studies and exploring the impact of their structure on the performance as a binder in LiB anodes. Their structural diversity makes this possible. The capability of the PILs to assist in the interfacial design of the SEI, its thickness and composition. Further, this study can also be extended to the other electrodes to improve the overall gravimetric capacity of LiBs. One of the chapters in this thesis explores silicon-based anodic materials and the results obtained has been promising. Silicon anodes are currently been seen as a potential replacement due to their very high gravimetric capacity. However, due to the uncontrolled SEI formation and pulverization on longer cycling which results in the capacity fade. Therefore, extending the current line of research to silicon anodes is very apt and will attract commercial attraction. Another attractive area to explore is to prepare N-doped carbon material from PILs and explore these interesting materials as anodic active materials in LiBs and Li-air batteries as catalysts. Due to their properties and ability to tune the properties based on structure, PIL based materials attract very high academic as well as commercial interest.

**Research Accomplishments**

**Publications:**


**Under preparation:**

1. Tejkiran Pindi Jayakumar, Rajashekar Badam, Noriyoshi Matsumi. “Effect of PIL Structure on its Performance as Anodic Binder in Li-ion Battery.”
2. Sai Gourang Patnaik, Tejkiran Jayakumar Pindi, Yukihiro Sawamura, Noriyoshi Matsumi. “Defined Poly(Borosiloxane) as an Artificial Solid Electrolyte Interface Layer for Thin-Film Silicon Anodes.”
3. Tejkiran Pindi Jayakumar, Kumar Sai Smaran, Badam Rajashekar, Noriyoshi Matsumi. “Silver Nanoparticles Doped rGO Interfaced Graphite Anodes for Li-ion Batteries.”
Abstract for formal hearing

Artificial deaminase system for restoration of genetic code

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Research Content

Site directed mutagenesis is an exceptionally viable way to deal with recode genetic information. Legitimate connecting of the synergist area of the RNA altering catalytic deaminase Adenosine Deaminase Acting on RNA (ADAR) or Cytidine Deaminase Acting on RNA (APOBEC) to an antisense direct RNA can change over explicit adenosines (As) to inosines (Is), with the last perceived as guanosines (Gs) during the translation procedure or Cytidines (Cs) to Uridines (Us). In this study, endeavors have been made to engineer the deaminase domain of ADAR1 and MS2 framework to target explicit A residues to reestablish G→A transformations. The target mRNA comprised of an ochre (TAA) stop codon, created from the TGG codon encoding amino acid 58 (Trp) of improved green fluorescent protein (EGFP). This framework had the capacity to change over the stop codon (TAA) to a decipherable codon (TGG), accordingly reestablishing fluorescence in a cell framework, as appeared by JuLi fluorescence and LSM confocal microscopy. The specificity of the editing was affirmed by Polymerase Chain Reaction-Restriction Fragment Length Polymorphism (PCR-RFLP), as the restored GFP mRNA could be cleaved into fragments of 160 and 100 base pairs, the absolute amplified length was 260 bp. Sanger’s sequencing illustration with both the sense and antisense primers indicated that the reclamation rate was higher for the 5'A than for the 3'A. This system might be very useful for treating genetic diseases that result from the G to A point mutations.

Further an artificial editase of RNA was engineered by combining the deaminase domain of APOBEC1 (apolipoprotein B mRNA editing catalytic polypeptide 1) with a guideRNA (gRNA) which is complementary to target mRNA. In this artificial enzyme system, gRNA is bound to MS2 stem-loop, and deaminase domain, which has the ability to convert mutated target nucleotide C-to-U, is fused to MS2 coat protein. As a target RNA, here RNA encoding Blue Fluorescent Protein (BFP) was used which is derivative of the gene encoding GFP by 199T>C mutation. Upon transient expression of both components
(deaminase and gRNA), GFP fluorescence was observed by confocal microscopy, indicating that mutated 199th C in BFP had been converted to U, restoring original sequence of GFP. This result was confirmed by PCR-RFLP and Sanger’s sequencing using cDNA from transfected cells, revealing an editing efficiency of approximately 21%. Deep RNA sequencing result showed that off-target editing was sufficiently low in this system.

Later on, improving U6 promoter activity by CMV enhancer or promoter in target cells have been demonstrated to be a viable method to obtain satisfactory percentage of editing efficiency. The placement of a CMV enhancer nearby to U6 promoter or hybrid CMV-H1 promoter has been accounted for improving the efficiency of RNAi or shRNA delivery in vivo. From the experimental data it has been found that in case of the CMV promoter controlled process of RNA editing where both the deaminase and guideRNA constructs were prepared under the control of the pol II CMV promoter, the editing efficiency was lesser comparing to the U6 promoter containing guideRNA or in single construct having combined approach of CMV in deaminase domain and U6 promoter in guideRNA construct. From the PCR-RFLP (band intensity) data had also been observed that with the increase of the concentration of the deaminase or the guideRNA the restoration percentage had also increased. The editing efficiency has been calculated from the peak height of the Sanger’s sequencing data. After the calculation of the efficiency it was found that in case of the CMV controlled approach the rate was 21.02% whereas in case of the U6 controlled and in case of single construct the restoration rate was 39.37% and 41.65%, respectively.

For performing the in vivo application of the developed artificial enzyme system the macular mouse model was chosen. The mutation in the P type copper transporting ATPase (ATP7A) gene is responsible for the Menkes kinky hair disease, where T-to-C mutation happens. It was found from our data that all the heterozygous female (Ml/+), normal littermate male (+/y) and hemizygous male (Ml/y) had increased the body weight as usual up to 10 days of age. After that the body weight of heterozygous female (Ml/+), normal littermate (+/y) and hemizygous male (Ml/y) had increased significantly at 14 days as well but in case of the hemizygous male (Ml/y), its body weight significantly reduced at 14th day of age. The peak area and peak height from the Sanger’s sequencing analysis was measured by ImageJ (NIH) software. From the calculation it was found that by using the APOBEC1 deaminase and U6-21bp upstream-MS2-6X guideRNA 12.17% and 16.25% of the genetic code was restored in the macular mouse derived
fibroblast cells by peak area and peak height, respectively. Where the deaminase and guideRNA, were two different constructs. After that single construct was applied where the deaminase was controlled by pol II CMV vector and guideRNA was under the control of pol III U6 promoter, in the same plasmid vector. The peak area and peak height from the Sanger’s sequencing analysis were measured by using ImageJ (NIH) software. From the calculation we found that by using the APOBEC 1 deaminase and U6-MS2-6X-21bp upstream 27.20% and 26.09% of the genetic code was restored, respectively calculated from peak area and peak height. Afterwards, the 1X MS2 on either side of guide sequence containing guideRNA construct was introduced along with the APOBEC 1 deaminase. Similarly the sample was sequenced for observing the editing rate. Editing rate was calculated both by peak area and peak height. I found that editing rate was 36.66% and 34%, respectively by peak area and peak height. For any developed system it is more important that the application could be achieved for the purpose of treatment.

**Research purpose**

The developed artificial deaminase system for both the A-to-I and C-to-U editing could be applied to the through the viral vector (AAVs) easily into the host body for the therapeutic purpose. The MS2 system along with the deaminase domain for the restoration of genetic code particularly C-to-U editing have been used for the first time both *in vitro* and *in vivo*. The proper application of the developed artificial deaminase system for the treatment of the patients who are suffering from such type of mutagenic diseases could open a new era in the field of genetic diseases.

**Key words:** Genetic code, RNA editing, Deaminase domain, ADAR1, APOBEC1, Macular mouse, ATP7A gene

**Research Accomplishment**

**Journal papers:**


3. **Sonali Bhakta**, Matomo Sakari and Toshifumi Tsukahara. RNA editing of BFP, a point mutant of GFP, using artificial APOBEC1 deaminase to restore the genetic code (Submitted-Scientific reports).


**Conferences attended:**
6. Poster: **Sonali Bhakta** and Toshifumi Tsukahara. RNA editing in BFP (derived from point mutated GFP) by using artificial APOBEC1 deaminase for genetic code restoration. JAIST Japan India Symposium, 2019.
Abstract

Structure-Dependent Electrical Conductance of Suspended Graphene Nanoribbon by In-situ Transmission Electron Microscopy Observation

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Doctor of Science (Materials Science)

1. Research Content

Background

Graphene, a two-dimensional (2D) monolayer of sp² hybridized carbon atoms arranged in a honeycomb lattice, has received significant attention due to its potential for use in electronic, biological, and optoelectronic applications[1–3]. However, bulk graphene is a zero band gap material and is thus unsuitable for nanoelectronic applications. A band gap can be engineered into graphene by fashioning it into nanoribbons, known as graphene nanoribbons (GNRs). One of the unique properties of GNR is that the electrical transport can be controlled by structure, i.e., width or edge structure. Especially, in the case of sub-10 nm wide GNR, the edge structure, zigzag or armchair, is critical to tune the electrical properties such as opening the band gap. The band gap of armchair-GNRs (AGNRs) has been reported to be caused by quantum confinement, while that of zigzag-GNRs (ZGNRs) is caused by spin polarization around the zigzag edges [4].

The structural dependence of band gap in GNRs has been investigated energetically by theories and experiments[5,6]. Both width and edge structure of the ribbon was reported to affect the band gap of GNR. However, the GNR fabricated on a substrate has been suggested to show significant suppress of predicted electronic properties due to the substrate dielectric screenings[7]. Thus, the electron transport properties of the GNR may change due to the substrate dielectric screenings. For solving this problem, in-situ transmission electron microscope (TEM) technique seems to be a suitable approach, since it realizes the observation and nano-scale modification of suspended GNR structure with simultaneous measurement of electrical conductance. However, the edge structure dependence of the electrical conductance behavior has not been clarified by in situ TEM observations.

Aim

In this thesis, a suspended GNR device is developed to realize a controllable GNR structure with an electron beam in aberration-corrected TEM (AC-TEM) and measure the width and electronic properties in situ. As shown in Figures 1a to 1c, this technique is realized using an in-house-built holder and substrate-free GNR device. The suspended GNR device is mounted on the TEM holder with electrical feedthroughs to measure the in situ electrical properties.
Figure 1. Experimental setup for in situ TEM observation with simultaneous electronic measurements. (a) Photograph of the in-house-built TEM holder. (b) Schematic illustration of the area around the head of the TEM holder with electrical connections. (c) Optical microscope image of the fabricated Si/SiN chip with electrodes. (d) TEM image of the gap fabricated at the center of an electrode. (e-f) TEM images of fabricated 102, 395, and 798 nm wide GNR, respectively.

**Experimental results**

The suspended GNR devices are fabricated with the width from ca. 100 to 800 nm, as shown in Figure 1e to 1g. After careful cleaning by current annealing, the suspended ribbon sculpt by convergent electron beam followed by a high bias annealing. During the thinning process, the measured I-V curves indicate that the electrical conductivity of ribbon change from metallic to semiconducting behavior, with the reduction of GNR width. When the width become very narrow (usually < 4 nm), the energy gap start to be opened. Figure 2 shows an estimated transport gap of 300 and 700 meV for 1.5 nm wide AGNR and ZGNR, respectively. The energy gap for ZGNR is more than two times larger than AGNR, although these two GNRs have the same width. Most importantly, the I-V curves for the ZGNRs are found to be obviously different from those for the AGNRs or mixture of both zigzag and armchair edges GNRs (MGNRs) as follows. (1) The ZGNRs showed a sharp increase at the threshold voltage in differential conductance-voltage curves. (2) The band gaps measured for ZGNRs were smaller than the band gaps calculated using the GW approximation. (3) The threshold voltage increased with the GNR length. These features support the previously theoretical expectation of current-driven magnetic-insulator and nonmagnetic-metal nonequilibrium phase transition, which is occurred by the application of a bias voltage. It suggests that narrow and short ZGNRs are thus good candidates for the fabrication of single nanosized switching devices.
2. Research Purpose

The structure-dependent electronic properties of suspended GNRs have been investigated by development of in situ TEM observation, which enable us to obtain structural information and simultaneous current-voltage curve measurements. By this development, the narrow GNRs could be controllable fabricated by convergent electron beam nanosculpting followed by high bias voltage annealing. I found that the suspended zigzag edge graphene nanoribbon with narrow width and short length shows a sharp increase (almost discontinuous change) at the threshold voltage in the differential conductance curve as a function of bias voltage, which has a potential for future nanosized switching devices. To my knowledge, such edge structure dependence of the electron transport property for suspended GNRs was obtained for the first time in the world. It is valuable to recognize the importance of edge structure. In addition, our developed in-situ TEM technique is also valuable, because it is promising for elucidating the structural dependence of electrical conduction in two-dimensional materials such as edge structure dependence.

3. Research Accomplishment

- **List of Publications**
  2. Chunmeng Liu, Jiaqi Zhang, Xiaobin Zhang, Muruganathan Manoharan, Hiroshi Mizuta,

• **Presentation**


**Reference**


Control of line tension at phase-separated domain boundary in lipid membranes

Materials Science, Takagi Lab, 1720435, Wongsirojkul Nichaporn

Part 1: Research Content

[Background]

The cell membrane is the fundamental structure to separate between inside and outside regions of the cell and maintain the survival of the cell by being the platform for several vital mechanisms. It consists mainly of various lipid species as the distinct of the cellular and physiological processes, and other molecules including peptides, proteins, and saccharides. From the raft hypothesis, it was believed that the particular interactions among sphingolipids, cholesterol, and membrane proteins provide the lateral compositional heterogeneity. The domain rich in saturated sphingolipids and cholesterol is defined as the raft region and the size of the domain is nanometer order. The cell membrane consists of the raft region and the surrounded region (non-raft) which is the more fluidity membrane consisting essentially of unsaturated sphingolipids. It was suggested that the modulation of raft organization relates to the regulation of the membrane-protein interaction, cell signaling, and membrane trafficking. Understanding the physicochemical properties of phase separation in the cell membranes might provide insights into cell homeostasis and survival of the cell. The cell membranes include so many kinds of molecules and the system is complex. In addition, the phase-separated domain in the cell membranes is nanometer scale and it is not visible by optical microscopy. Therefore, it is difficult to study the nano-sized phase separation in the vital cells.

Phospholipid, a typical amphiphilic molecule, is a main component of cell membranes. Phospholipids self-assemble into bilayer structure in water by the hydrophobic interactions. Bilayer is a fundamental structure of cell membrane and it can be regarded as a model cell membrane. In multi lipid component membranes, micron-sized phase-separated domains emerge. The typical phases at room temperature are a solid-ordered (S_o) phase which is rich in saturated lipids, a liquid-ordered (L_o) phase which is rich in saturated lipids and cholesterol, and liquid-disordered (L_d) phase composed largely of unsaturated lipids. At higher temperature, all lipids mix uniformly. In order to reveal the mechanism of raft domain formation, many studies on the phase separation in these model cell membranes have been performed widely.

Line tension becomes an important physical value to evaluate the stability of phase separation. Line tension is an interfacial tension at phase-separated domain boundary. Atomic force microscopy (AFM) and x-ray scattering determinations showed that the thickness between L_o and L_d phases is different and there is height mismatch of lipids at the domain edge. The energy cost resulting from height mismatch is the source of line tension. The increase of hydrophobic mismatch can rise the line tension and the size of domains. On the contrary, when the
line tension becomes smaller, the domain becomes smaller, the domain shape fluctuates, and finally the domain disappears. Therefore, the control of line tension can regulate phase-separated structures.

In this thesis, the line tension is regulated by two systems. First, we modulate the vesicles by the application of osmotic pressure. It was reported that the phase separation is enhanced to occur against the osmotic pressure. However, the exact physicochemical mechanism behind remains elusive. The effects of osmotic pressure on the line tension might be beneficial to understand the insight mechanism and also better understand the response of cell membranes for the homeostasis and survival of the cells. Second, we modulated the line tension using the addition of monounsaturated fatty acids (MUFA). Oleic acid (OA) is the common MUFA abundantly found in olive oil. It is profitable to decrease low-density lipoprotein and lower the risk of cardiovascular disease. Interestingly, it was reported that OA can decrease the line tension at the domain boundary. Therefore, it is very interesting to study the effects of the cis position and chain length of these MUFA on the line tension. Results might be advantageous to understand the more precise control of phase separation based on these two methods.

[Aim]

The effects of osmotic pressure on phase separation and miscibility temperature in lipid membranes consisting of dioleolylphosphocholine (DOPC)/ dipalmitoylphosphocholine (DPPC)/ Cholesterol (Chol) were investigated. Also, we compared the consequences of osmotic pressure on the line tension at the domain boundary between DOPC/DPPC/Chol and diphytanoylphosphatidylcholine (DiphyPC)/DPPC/Chol. In the last part, we showed the modulation of the line tension by the addition of the fatty acids and also the application of osmotic pressure in the mixed lipid membranes.
**Experimental Results**

We showed the extended area of phase separation in the ternary phase diagram upon the osmotic pressure. It was also found that osmotic pressure can shift the miscibility temperature which is the transition temperature between phase separation and homogeneous phase. Interestingly, the shift of the miscibility temperature is greater in the higher content of cholesterol. Furthermore, osmotic pressure can encourage the increase of line tension in both DOPC/DPPC/Chol and DiphyPC/DPPC/Chol system similarly. The plausible mechanism was also proposed that the osmotic pressure mediated membrane tension suppresses the membrane fluctuation and causes the change of free energy.

For the modulation of line tension by the effects of chemical stimuli, we compared five different monounsaturated fatty acids based on their differences in chain length and the position of cis configuration. Regarding their physical properties and our findings, we can categorize their behaviors in the lipid membrane into two types: Oleic acid type and Palmitic acid type. The oleic acid type fatty acids can mainly partition in the L_d phase and some amount of them can include in the L_o phase and disturbing the hydrophobic chain of the L_o phase. The palmitic acid type of fatty acids partition in the L_o phase and act differently from the Oleic type. They strongly interact with DPPC and exclude the cholesterol from the L_o phase. Therefore, the S_o/L_o phase can be produced by the effects of the palmitic acid type of fatty acid. Additionally, we also showed an increase of line tension of mixed lipid membranes due to the osmotic pressure.

Our results provide the insight into biophysics of cell membranes how cell responses and survive upon the osmotic pressure. The modulate of line tension against both osmotic pressure and the addition of unsaturated fatty acids can be an insightful model to understand the phase separation of the cell membranes.
Part 2: Research Purpose

Cell membranes play a vital role in homeostasis to maintain the living of cells against several external stimuli. Failure of maintaining homeostasis of the cell membrane leads to reduction of biofunctions and cell death. It is very interesting to find out how the lipid membrane itself acts against the external stimuli for cell survival. Phase separation naturally occurs from the lipid-lipid interaction. Understand of the phase separation might provide insights into the biophysics mechanisms of the response of the cell membranes. Studies on the endothelial cells showed that the lipid membrane responds differently against different physical stimuli such as stretch, stress, and osmotic pressure. Interestingly, the response of endothelial cells against the osmotic pressure is similar to those of the artificial vesicles. Also, it was reported that the phase separation in model membranes is enhanced against the osmotic pressure. However, the mechanism behind is still unknown. Herein, we would like to understand the response of lipid membranes upon external stimuli. We showed effects of osmotic pressure on the phase separation, miscibility temperature, and also line tension. The probable mechanism of the enhance of phase separation due to osmotic pressure is also discussed. As the line tension is the vital parameter to control the phase separation and domain size. Also, our study showed the modulation of line tension by both physical and chemical stimuli. We compared the effect of chemical structure in terms of the chain length and the cis position of the monounsaturated fatty acid on the line tension and transition temperature. For the addition of monounsaturated fatty acid, we can classify them as two types due to their behaviors in the lipid membranes. Also, we showed the enhance of line tension on the fatty acid mixed lipid membranes by the application of osmotic pressure. This work assisted to understand the mechanism of the bilayer membranes and domain stability response upon both physical and chemical stimuli. The lipid membrane provides the mechanosensor to respond differently against various stimuli. In advance, it is curious to alter the cholesterol content in monounsaturated fatty acid mixed lipid membranes. Also, the study of cholesterol oxidation regarding aging on the artificial model is much attractive.

Part 3: Research Accomplishment

[Paper]
- Modification of line tension in mixed lipid membranes – *Manuscript in preparation*

[Academic meetings]
Thermal Transport in Suspended Graphene Phononic Crystal (GPnC)

Doctor of Science (Materials Science)

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a. Research content

Background

With the advances in the field of electronics, it has become relevant to reflect on the ever-growing problem of management of waste heat and probe further into nanoscale heat transport as the devices are being vigorously scaled down to tens of nanometers. The physical entity that can help create thermal blockade is now defined as phononic crystals (PnCs) in the community- the terminology rooted into the word ‘phonon’ which represents the quanta of atomic vibration in materials. Fabrication of PnCs has become a subject of interest for the potential it offers for heat propagation control. Fabrication of intricate nanopatterns on materials like silicon and steel has long since been realized with the optimization of various focused ion beam (FIB) techniques. However, it has been reported that, with superior physical and mechanical properties i.e. Young’s modulus (~1 TPa) and Debye temperature (~1900 K) graphene offers better flexibility and control of phonon contributions. In this work, we have reflected on the asymmetry in thermal transport in graphene phononic crystals as an initial study to understand thermal rectification characteristics in nanoscale devices.

Summary of results

First, the dispersion curves and transmission probability of graphene based phononic crystals by configuring different periodicity, porosity and pore shape were studied by Finite Element Method simulations. From the dispersion relations, obvious band flattening or distinct frequency regions were observed where phonon transmission was completely blocked. The analysis showed strong evidence of porosity and pore shape dependency on phononic band gap (PnBG) generation. For circular shaped nanopores, a very small PnBG opens at ~0.4 THz only at a high porosity over 0.73 which is extremely difficult to achieve using the current experimental facilities. To address this limitation, cross shaped nanopore pattern was introduced where PnBG opened at a porosity ~0.28. The PnBG was most obvious at ~0.9 THz for single nanometer neck length and completely disappeared when it increased to 10 nm indicating that the constrictions due to the narrow neck structure induced phonon modes confinement contributing to the suppression or flattening of the dispersion relation. At similar porosity and unit cell size, snowflake shaped pores exhibited phononic bandgap (PnBG) in gradually higher THz (~1.5 THZ) regime as the symmetric placement of the neck
length along all the supercell edges reinforced the phonon confinement. Also, the snowflake shaped nanopattern gives the advantage of having larger neck lengths of $\sim 10$ nm (fig. 1). 

Next, a reproducible hybrid method was developed and demonstrated to successfully fabricate large area (in $\mu$m$^2$ dimensions) suspended graphene nanomesh (GNM). The GNR are patterned into required dimensions using EBL and later suspended by buffered hydrofluoric acid (BHF) release with gold electrodes acting as a heater. The GNM is fabricated by milling periodic nanopores with as small as $\sim 6$ nm diameter on the suspended GNR by direct focused helium ion beam milling (HIBM). Taking advantage of the fidelity of HIBM, symmetric and asymmetric graphene nanomesh (GNM) samples were fabricated. As asymmetric GNM with nanopores patterned on half of the total area of the GNR is shown fig. 2(a). The concept of resistive thermometry was used to develop a 4-probe measurement method for thermal characterization of the prepared GNM devices which had 20 nm, 25 nm and 30 nm pitch and $\sim 6$ nm diameter nanopores. With the base temperature maintained at 150K in a cryogenic vacuum probe station, joule heating was used to generate temperature at the metal electrode. With the measurement setup, resistance at the electrode was measured accurately and the corresponding temperature was calculated. By observing the change in temperature at the heater when there is GNM present, it was confirmed that some of the heat is dissipated through the GNM. The measurement was adopted to observe the trend of thermal dissipation through asymmetric and

\[ \text{Figure 1: Calculated dispersion relation for cross-shaped and snowflake-shaped nanopores with 28\% porosity maintained for both cases.} \]
symmetric GNM by maintaining similar experimental conditions and most interestingly, characteristics of thermal rectification by introducing asymmetry in the GNM was observed when the heater position was changed. It was observed that the heat transport through the non-meshed area of the patterned GNR to the meshed area is larger compared to when the heater position is swapped and heat transport direction is from the meshed area to the non-meshed area (fig. 2(b))

![Figure 2: (a) Suspended asymmetric GNM device with nanopores patterned on half of the entire GNR area. (b) Qualitative analysis of asymmetry of thermal transport for the fabricated device.](image)

b. Research objective

Controlling the thermal conductivity of a material independently of its electrical conductivity has always been an intriguing aspect for practical applications of thermoelectric materials. Research on thermal rectification is very important to establish the idea of controlling current induced heat transfer. Numerical simulations performed using continuum models of graphene PnCs in the COMSOL multiphysics platform provided the initial ideas and information to fabricate the GPnC device. A hybrid method by incorporating electron beam lithography (EBL) and helium ion beam milling (HIBM) was developed to fabricate graphene nanomesh (GNM) devices to study their thermal transport characteristics. A 4-terminal thermoelectric measurement method was established to detect the thermal transport through the fabricated GNM. This work provides the initial knowledge and ideas that could provide important information to the community to fabricate graphene based devices for thermal rectification applications.

c. Research accomplishment

Academic journals


International conferences

1. Phononic bandgap formation in single nanometer graphene nanomesh
   **Mayeesha Haque**, M. E. Schmidt, M. Muruganathan, I. Katayama, J. Takeda, S. Ogawa, H. Mizuta
   The 1st JAIST World Conference (JWC2018), Nomi, 27-28 February 2018 (Poster presentation)

2. Phononic Bandgap Engineering in Single Nanometer Graphene Nanomesh
   Joint Conference of the 16th International Conference on Phonon Scattering in Condensed Matter (Phonons 2018) and the 4th International Conference on Phononics and Thermal Energy Science (PTES 2018), Nanjing, China, 31 May - 3 June 2018 (Oral presentation)

National conferences (in chronological order)

1. Effects of structural dimensions on phonon bandgaps in nanopatterned graphene phononic crystals
   **Mayeesha M. Haque**, Marek E. Schmidt, Takuya Iwasaki, Manoharan Muruganathan, Hiroshi Mizuta
   第 78 回応用物理学会秋季学術講演会

2. Graphene Nanophononics: Sample fabrication and FEM Simulation I
   **Mayeesha M. Haque**, Seiya Kubo, Marek E. Schmidt, Manoharan Muruganathan, Shinichi Ogawa, Hiroshi Mizuta
   第 2 回フォノンエンジニアリング研究会
   2018 年 7 月 13 日-14 日、KKR ホテル熱海

3. Fabrication process and thermal conductivity measurement setup of graphene phononic crystal
   **M. Haque**, S. Kubo, M. E. Schmidt, M. Muruganathan, S. Ogawa, H. Mizuta
   第 79 回応用物理学会秋季学術講演会
   2018 年 9 月 18 日-21 日、名古屋国際会議場

**Keywords:** Graphene phononic crystal, Graphene nanomesh, Helium ion beam milling, Phononic bandgap, Resistive thermometry, Thermal rectification.