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FEATURE STORY

Tackling Water Pollution, a Sustainable Development Goal (SDGs)

Easily and accurately measuring phosphorus, the cause of eutrophication

Harmful growth of plankton causes the oceans and tides to turn red. Hypoxia that develops in enclosed bays creates frothy blue water.

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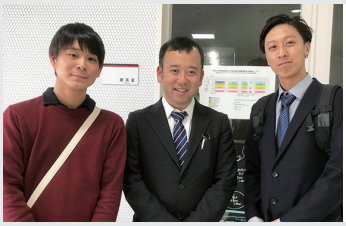

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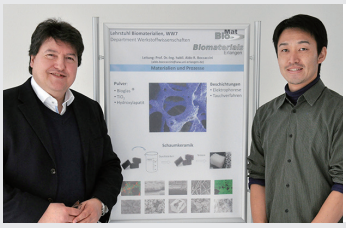

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Tackling Water Pollution, a Sustainable Development Goal (SDGs)

Easily and accurately measuring phosphorus, the cause of eutrophication

Takanobu Inoue

Harmful growth of phytoplankton causes the oceans and tides to turn red. Hypoxia that develops in enclosed bays creates frothy blue water. Micro-algae in lakes leads to algal growths that cover large areas of the water's surface. All of these issues indicate serious damage to water quality and lead to the mass death of marine life. This is due to eutrophication, which is caused by an imbalance in nutrients such as nitrogen and phosphorus. Among these nutrients, Professor Takanobu Inoue focuses on phosphorus. After identifying bioavailable phosphorus, he looked at actual on-the-ground conditions and devised an extremely simple and effective measurement method to help reduce runoff.
This research contributes to the achievement of the Sustainable Development Goal 14: Life below water — Conserve and sustainably use the oceans, seas and marine resources for sustainable development.

Interview and report by Madoka Tainaka

Eutrophication: A Cause of Major Water Quality Issues

Nutrients such as nitrogen and phosphorus are essential to the survival of plants and organisms. In particular, since there is no phosphorus in the atmosphere, plants and organisms have long relied on water that contains phosphorus derived from forests, sharing these resources in a way that maintains a balanced ecosystem. However, Professor Inoue notes that in recent years, this balance has been significantly disturbed due to issues with water quality.

"Many people live on river basins, and excessive volumes of nitrogen and phosphorus flow through the rivers into enclosed bodies of water. Organic matter consumes oxygen and decomposes, and nutrients accumulate at the bottom," says Inoue. "Moreover, the consumption of oxygen results in hypoxia, which is the condition of extremely low oxygen levels. This hypoxia rises to the surface, causing blue discoloration. The high concentration of nutrients causes various problems such as red tides and algal blooms.

"In Japan, the algal bloom at Biwa Lake in the 1970s is particularly well-known. In order to address the issue and decrease the corresponding nitrogen and phosphorus, Shiga Prefecture enacted the Ordinance for the Prevention of Eutrophication of Lake Biwa in 1979, prohibiting the sale of synthetic detergents containing phosphorus along with enforcing drainage regulations on factories. The passage of this regulation led various detergent manufacturers to begin selling non-phosphate detergents, leading to the improvement of water quality nationwide. However, today, algal blooms are not just limited to Lake Biwa. Almost every year, red and blue tides occur in places like Mikawa Bay and Tokyo Bay. And it's not just Japan. Eutrophication is becoming a major environmental issue across the world," says Inoue.

Runoff from Agricultural and Urban Areas is the Cause

Ministry of the Environment regulations limiting runoff load are required in order to manage the runoff of nutrients into rivers. Runoff calculations intended for such regulations conducted in a study of Mikawa Bay revealed that the total phosphorus-generating load (t/day) in 1999 was 4.3% of domestic and industrial wastewater. In 2003, this figure dropped to 2.4%, which, along with nitrogen, marked a significant improvement.

However, measurements across multiple locations in Mikawa Bay showed that nitrogen and total phosphorus levels remain relatively unchanged, with many areas not meeting environmental standards. Why is this?

Fig.1 Agricultural land during rainfall

"Regulations for sewage and industrial water treatment became more stringent, and the prescribed measurement method shows the total load decreasing. However, there appears to be another factor preventing the levels from falling.

"We decided to focus on nutrient salt runoff during rain events. From 2009 to 2011, we conducted a study of the Hamada River, one of the channels flowing into Mikawa Bay. Measurements were taken at a fixed time every month and ten times after it rained. Measurement results showed that while the total phosphorus amount was 0.52% (t/km2/year) when using the prescribed measurement method, the actual value was 3.65%. In other words, phosphorus runoff was seven times the regulation load," explains Professor Inoue.

This was due to the breakdown of runoff sources. Up to that time, total load regulations assumed that approximately 90% of runoff came from discrete sources such as factory and domestic drainage. In fact, total phosphorus from diffuse sources such as agricultural and urban areas accounted for nearly 90% of runoff.

"One factor in this discrepancy is that the measurement method used for total load regulations did not alter the output levels of diffuse sources since it began in 1988. In other words, the idea that strictly regulating factory and domestic drainage would suppress eutrophication was incorrect. In particular, runoff load during rain events is believed to result in a high volume of fertilizer runoff from agricultural areas. It is also possible that livestock waste at small-scale cattle ranches flows into rivers during rain events. Runoff in urban areas is also significant. Eutrophication can only be stopped if runoff from diffuse sources can be reduced," says Inoue.

Finding out Which Particulate Phosphorus is Bioavailable

On the other hand, Professor Inoue says that while current regulations target total phosphorus, not all phosphorus is bioavailable.

"While some dissolved phosphorus in the water can be used by algae for growth, algae can use some particulate phosphorus (granular phosphorus mixed with various substances). As there is a particularly large runoff of particulate phosphorus when it rains, when it comes to eutrophication, it is critical to measure the bioavailable phosphorus. In doing so, it becomes necessary to change the way we capture it, as seen with the 3.65% measurement discovered in our previous survey of Hamada River."

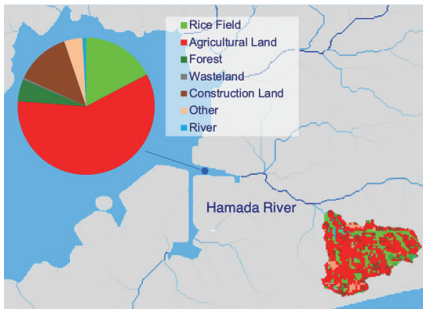


Fig.2 Measurement of nutrients runoff from rain at the Hamada River

Typically, particulate phosphorus is measured using a shake extraction method that takes up to 17 hours. However, Professor Inoue discovered a simple method that uses ultrasonic to divide and extract the bioavailable phosphorus from the particulate phosphorus in as little as one minute. This method was inspired by separate research, in which ultrasonic was used to extract available phosphorus in soil used by plants.

This method was used in a study of the Umeda River and the Yagyu River flowing through Toyohashi City. While total phosphorus in the Umeda River was higher, the Yagyu River had higher concentrations of bioavailable phosphorus. "97% of the water in the Umeda River basin comes from farmland. The concentration of total phosphorus is high due to fertilizer runoff from the farmland. However, the load of dissolved phosphorus flowing into the river is not particularly high since much of the fertilizer in the soil is consumed on-site by organisms. The particulate phosphorus, coupled strongly with the iron and calcium contained in high concentrations in the soil, also cannot be used again by organisms. As such, the amount of phosphorus that can be consumed by organisms is relatively low. At the same time, the large load of particulate phosphorus that flows from forests during rain is already being used by plants and organisms, so there is little effect on eutrophication downstream.

"On the other hand, 73% of the water in the Yagyu River comes from urban areas. Since large areas are covered in asphalt, the nutrients flow straight into the rivers. This causes phytoplankton and other organic matter to grow. In other words, the concentration of bioavailable phosphorus is greater.

"It is increasingly clear that existing regulations on total phosphorus are insufficient. Moving forward, I hope to conduct a more detailed study on how organisms actually use phosphorus," says Inoue.

Professor Inoue's initiatives have shown that, despite the tendency to classify phosphorus into one category, there are significant differences in the ratio of bioavailable phosphorus depending on each region's characteristics.

Solving water problems is one of the SDGs adopted by the United Nations, and dealing with eutrophication is an urgent issue. Moving forward, it will be necessary to review the measurement methods of regulation loads and implement policies based on actual on-the-ground conditions.

Reporter's Note

Takanobu Inoue was born in Otsu, Shiga Prefecture. As a high school student, he witnessed issues with Biwa Lake's water quality. Hoping to help, he entered Hokkaido University's Department of Sanitary Engineering. Beginning by focusing on the impact to the ecosystem, he then shifted to a focus on human health, one of the original goals of sanitary engineering.

"Half of the students in the lab are foreign exchange students from Asia. Their home countries are dealing with problems such as mercury poisoning from gold mining and E. coli in drinking water. I am involved in working with the foreign exchange students on related studies.

"This year, we began a study examining the amount of plastic flowing into the ocean in Indonesia. In looking at issues such as how to limit the source for microplastics, it is clear that we have a significant mission in our society," says Inoue. I have kept the same goal since I was a high school student. I am still working every day to improve our water.

Fig.3 Fieldwork in Indonesia

水環境問題の解決でSDGsの達成に貢献

富栄養化の原因となるリンをより簡便に正確に計測

植物プランクトンの異常増殖により海水や湖水が赤く変色する赤潮や、閉鎖的な内湾などで発生した貧酸素水塊によって海水などが白濁する苦潮（青潮）、湖沼などで微細藻類が大量発生して水面を覆い尽くすアオコ（青粉）――いずれも、魚介類の大量死などを招く深刻な水質汚染である。その原因は、窒素やリンなどの栄養塩類による富栄養化にある。井上隆信教授は、栄養塩のうち、とくにリンに着目して、生物が利用可能なリンを見分け、実態に即した排出削減などに役立てるために、極めて有効で簡便な計測方法を見出した。

深刻な水質問題の原因となる富栄養化

窒素やリンなどの栄養塩は、そもそも動植物の生存に欠かせない物質である。とくにリンは大気中には存在しないため、動植物は太古の昔から森林などから流出したリンが含まれる水を利用して、それぞれ分け合いながら、生態系のバランスを保ってきた。しかし、近代以降、そのバランスが大きく崩れたことが、現代の水質問題を生んできたと、井上隆信教授は指摘する。

「河川流域に多くの人が住み、河川を通じて閉鎖性水域へ多くの窒素やリンが過剰に流入し、有機物が酸素を消費して分解して栄養塩類が底に溜まります。さらにこれが酸素を消費するため、極端に酸素の少ない貧酸素水塊が発生します。この貧酸素水塊が表層に上がってくることで、苦潮が生じたり、栄養塩濃度が高くなることで赤潮やアオコが発生するといったさまざまな問題が噴出するようになってきました。

日本ではとくに1970年代の琵琶湖のアオコ問題が有名です。この問題を受けて、原因物質である窒素やリンの排出を減らすため、滋賀県は1979年に「琵琶湖富栄養化防止条例」を制定し、工場などへの排水規制と合わせて、リンを含む合成洗剤の販売を禁止しました。これがきっかけとなって、各洗剤メーカーが無リン洗剤を発売するようになり、水質は全国的に改善に向かったように見えます。しかし、いまも琵琶湖のアオコに限らず、三河湾でも東京湾でも、毎年のように赤潮や苦潮が発生している。日本だけでなく、富栄養化は世界的にも深刻な環境問題となっています」

農耕地や市街地からの流入が原因

そのために必要な措置が、栄養塩を河川などに流入させないための環境省の総量規制である。三河湾流域の調査における総量規制の算定法による結果では、平成11年の全リン発生負荷量（t/日）は、生活排水や産業排水などを合わせ4.3%だったが、平成15年では2.4%と、窒素同様にかなり減った結果となっている。

一方で、実際の三河湾数カ所での実測値では、窒素も全リンの濃度も横ばいのままであり、環境基準を満たさない水域が多くを占めた。これはなぜか。

「下水処理や産業系の処理水の基準は厳しくなっているので、総量規制の計算上は減っていることになっていますが、別の要因で減っていないことが考えられます。

そこで我々が着目したのが、降雨に伴う栄養塩類の流入です。三河湾に流入する河川の一つである浜田川を対象に、2009年から2011年まで、月1の定期検査と降雨時に10回の調査を行いました。その結果、全リンについては、総量規制の算定法による負荷量（t/km2/年）が0.52%であるのに対して、実測値では3.65%であることがわかりました。つまり、総量規制の7倍ものリンが流入していたのです」と井上教授は説明する。

その理由は、排出源の内訳にあった。これまで総量規制では工場排水や生活排水など「点源」と呼ばれる排出源が約9割を占めるとみなしてきたが、実際には、農耕地や市街地など「面源」と呼ばれる排出源からの全リンの流入が9割近くを占めていたのである。

「これは、総量規制の算定法が、1988年の開始当初から面源の原単位が変更されていないことが一因です。つまり、工場排水や生活排水の規制を厳しくすれば富栄養化が抑制できるという考え方自体が間違いでした。とくに降雨時には、農耕地から肥料が大量に流出することが考えられますし、小規模な畜産場では、糞尿が降雨時に河川に流入している可能性があります。市街地からの流入もかなりある。面源から入ってくる流入量を減らさない限り、富栄養化に歯止めはかかりません」

懸濁態リンのうち生物利用可能態リンを明らかに

一方で、井上教授は、総量規制では全リンが対象とされているが、リンのすべてが生物に利用されるわけではない、と言う。

「水中のリンのうち、溶存態リンは生物が増殖に利用できる生物利用可能態リンですが、懸濁態リン、つまりさまざまな物質と結合した顆粒状のリンについては、生物が利用できるのは一部です。とくに降雨時には懸濁態リンが大量に流入するため、富栄養化の観点から見れば、生物利用可能態リンの計測が重要になる。そうなると、先の浜田川の調査で明らかにした3.65%という数字についても、捉え方を変える必要があります」

従来、懸濁態リンの計測には、17時間にもおよぶ振とう抽出法が採用されてきたが、井上教授は懸濁態リンから生物利用可能態リンだけを抽出する方法として超音波を用いて、わずか1分間程度の分解・抽出ができる簡便な手法を見出した。この手法は、別の研究の際、植物が活用する土壌の「可給態リン」の抽出に用いる超音波法からヒントを得たものだという。

この方法を使い、豊橋市を流れる梅田川や柳生川で調べたところ、全リンでは梅田川のほうが比率は高かったが、生物利用可能態リンの観点では、柳生川の方が比率が高いことがわかった。

「梅田川流域は97%が農地で、農地から流入する肥料などによる影響から全リンで見れば比率が大きくなります。ところが、土壌に撒かれた肥料の多くはその場で生物に利用されるため河川に流出する溶存態リンの量はさほど多くはなく、土壌には鉄やカルシウムが多く含まれていて、これらと強く結合した懸濁態リンもまた生物には利用されないので、生物利用可能という観点で見れば比率が少なくなるのでしょう。同様に、降雨時には森林からも懸濁態リンが大量に流入しますが、すでに生物や植物に使われているため、下流の富栄養化にはほとんど影響しません。

一方、柳生川流域は73%が市街地であり、アスファルトに覆われた地域が多いため、栄養塩はそのまま河川に流入します。これにより植物プランクトンなどの有機物が増殖する。つまり生物に利用されるリンの比率が多くなる、と考えられます。

そうなるとますます、従来の全リンによる総量規制では対策が不十分であることがわかります。今後はさらに、実際に生物にどの程度、リンが利用されているのか詳細に調べたいと思っています」と井上教授は語る。

このように、井上教授らの取り組みにより、一口にリンといっても、地域の特性ごとに、生物利用可能態リンの割合には大きな違いがあることが解明されつつある。

水環境問題の解決は、国連が掲げるSDGsの一つでもあり、富栄養化対策は喫緊の課題である。今後は総量規制の算定法の見直しも含めて、より実態に即した対策を打っていく必要があるだろう。

（取材・文＝田井中麻都佳）

取材後記

滋賀県大津市出身の井上教授。ちょうど高校生の頃に、琵琶湖の水質問題に直面し、その改善に貢献したいと、北海道大学衛生工学科へ進学したという。当初は生態系への影響を対象としていたが、しかしいまは、衛生工学が当初目的としていた人の健康を対象にし始めている。

「研究室はアジアからの留学生が半数を占めていますが、そうした国々では、鉱山での採掘に伴う水銀被害や飲料水の大腸菌汚染などが問題となっています。そうした調査も留学生とともに手がけています。

今年から、インドネシアで海洋へのプラスチックの流出量を調べる調査も始めました。問題となっているマイクロプラスチックの元をいかに防ぐのか、社会的使命は大きいと思っています」と井上教授。高校生のときに抱いた志はいまも変わることなく、水環境の改善に日々、努めている。

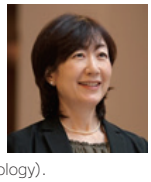
Researcher Profile

Dr. Takanobu Inoue

Dr. Takanobu Inoue received his M.S. and PhD degree in engineering in 1986 and 1996 respectively from Hokkaido University, Japan. He was researcher in 1986 and senior researcher in 1994 at National Institute for Environmental Studies. In 2000, he joined Gifu University as a assosiate professor. Since he started his career at Toyohashi University of Technology in 2004, had been involved in water environment engineering and sanitary engineering. He is currently a professor at the Department of Architecture and Civil Engineering, Toyohashi University of Technology.

Reporter Profile

Madoka Tainaka is a freelance editor, writer and interpreter. She graduated in Law from Chuo University, Japan. She served as a chief editor of "Nature Interface" magazine, a committee for the promotion of Information and Science Technology at MEXT (Ministry of Education, Culture, Sports, Science and Technology).

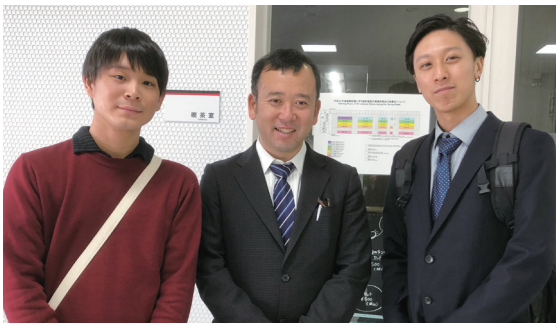


Progress Towards the Realisation of Advanced Higher Capacity Li-ion Batteries

Binder-less tin phosphide/carbon composite film electrodes by aerosol deposition process

by Ryoji Inada

Associate Professor Ryoji Inada and his research team at the Toyohashi University of Technology have successfully fabricated a binder-less tin phosphide (Sn_4P_3)/carbon (C) composite film electrode for lithium-ion batteries via aerosol deposition. The Sn_4P_3/C particles were directly solidified on a metal substrate via impact consolidation, without applying a binder. Charging and discharging cycling stabilities were improved by both complexed carbon and a controlled electrical potential window for lithium extraction. This new material could help realize advanced lithium-ion batteries of higher capacity.



Associate Professor Ryoji Inada (Center) and his students

Lithium-ion (Li-ion) batteries are widely used as a power source in portable electronic devices. They have recently attracted considerable attention because of their potential to be employed in large-scale uses, such as acting as a power source for electric vehicles and plugin hybrid electric vehicles, and as a stationary energy storage system for renewable energy. To realize advanced Li-ion batteries with higher energy density, anode materials with higher capacity are required. Although a few Li alloys such as Li–Si and Li–Sn, whose theoretical capacity is much higher than that of graphite (theoretical gravimetric capacity = 372 mAh/g), have been extensively studied, they generally result in poor cycling stability due to the large variation in volume during charging and discharging reactions.

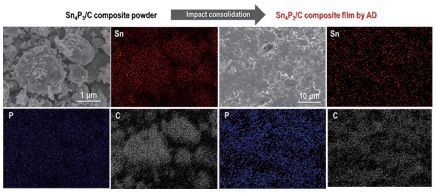


Fig.1 Scanning electron microscope (SEM) images of Sn_4P_3/C composite particles (1st row:1st image), and surface of Sn_4P_3/C composite film fabricated by the AD process (1st row:3rd image). Corresponding elementary distributions for Sn, P, and C are also shown.

Tin phosphide (Sn_4P_3) (theoretical gravimetric capacity = 1255 mAh/g) with layered structure, generally used as a high-capacity alloy-based anode material for Li-ion batteries, has an averaged operational potential of ~0.5 V vs. Li/Li+. Reports indicate that complexing carbon materials with nano-structured Sn_4P_3 particles significantly enhance the cycling stability. Generally, electrodes used in batteries are fabricated by coating a slurry consisting of electrode active materials, conductive carbon additives, and binders, on metallic foils. For carbon complexed Sn_4P_3 (Sn_4P_3/C) anodes (such as those reported in the literature), the weight fraction of the active materials in an electrode is decreased by approximately 60~70 % because of the use of significant quantities of conductive additives and binders to achieve stable cycling. Consequently, the gravimetric specific capacity per electrode weight (including those of conductive carbon additives and binders) is decreased significantly.

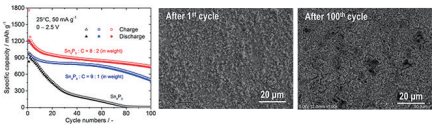


Fig.2 Cycling performance of Sn_4P_3 and Sn_4P_3/C composite films for different carbon contents (left) in a two-electrode cell with Li metal as the counter electrode. Cycling test was performed at cell voltage windows ranging from 0 V to 2.5 V. SEM images of Sn_4P_3/C composite film surface after the 1st (middle) and 100th cycles (right) are also shown.

Associate Professor Ryoji Inada and his research team at the Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, have successfully fabricated a binder-less Sn_4P_3/C composite film electrode for Li-ion battery anodes via aerosol deposition (AD). In this process, the Sn_4P_3 particles are complexed with acetylene black using a simple ball-milling method; the obtained Sn_4P_3/C particles are then directly solidified on a metal substrate via impact consolidation without adding any other conductive additives or binders.

This method enables enhancement of the fraction of Sn_4P_3 in the composite to above 80%. Furthermore, structural change of the composite electrode is reduced and cycling stability is improved by both complexed carbon and a controlled electrical potential window for lithium extraction reaction. The Sn_4P_3/C composite film fabricated by the AD process maintains gravimetric capacities of approximately 730 mAh g-1, 500 mAh g-1, and 400 mAh g-1 at 100th, 200th, and 400th cycles, respectively.

The first author Toki Moritaka is quoted as saying, “Although optimizing the deposition conditions was difficult, useful information on enhancement of cycling stability of the Sn_4P_3/C composite film electrode fabricated by the AD process was obtained. The complexed carbon functions not only as a buffer to suppress the collapse of electrodes caused by the large variation in the volume of Sn_4P_3, but also as an electronic conduction path among the atomized active material particles in the composite.”

“This process is an effective means to increase the capacity value per electrode weight. We believe there is scope for improvement of the electrochemical performance by the size and content of the carbon in Sn_4P_3/C used in composite film fabrication by the AD process. We are now trying to optimize the complexed carbon content and increase the composite film thickness,” quotes Associate Professor Ryoji Inada.

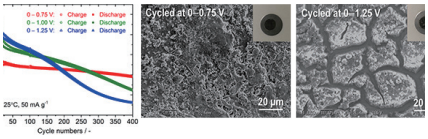


Fig.3 Long-term cycling performance of Sn_4P_3/C composite films at different cell voltage windows ranging from 0 V to 0.75 V, and that from 1 V and to 1.25 V (left). SEM images of Sn_4P_3/C composite film surfaces cycled at 0 V 0.75 V (middle) and that at 0 V 1.25 V (right) are also shown.

The findings of this study may contribute to the realization of advanced Li-ion batteries of higher capacity. Moreover, because not only Li but Na can also be stored in and extracted from Sn_4P_3 by similar alloying and dealloying reactions, the Sn_4P_3 electrode can be employed in next-generation Na-ion batteries at much lower costs.

This work was partly supported by Grant-in-Aids for Scientific Research (Grant No. 16K06218 and 16KK0127) from the Japan Society for the Promotion of Science (JSPS).

Reference

Toki Moritaka, Yuh Yamashita, Tomohiro Tojo. Ryoji Inada, Yoji Sakurai (2019). Characterization of Sn_4P_3-Carbon Composite Films for Lithium-Ion Battery Anode Fabricated by Aerosol Deposition: Nanomaterials, 9(7), 1032.10.3390/nano9071032. http://dx.doi.org/10.3390/nano9071032

Pupillary Response to Glare Illusions of Different Colors

A blue glare illusion was perceived as brightest and caused larger pupil constriction

By Yuta Suzuki

The Department of Computer Science and Engineering at Toyohashi University of Technology formed a research team with the University of Oslo to measure the size of subjects' pupils when viewing a brightness illusion (glare illusion). The pupil expands in dark environments and contracts in bright environments in order to control the amount of light that enters the eye. Pupil contraction is also known to occur when people feel that a viewed object is brighter, even though this may not be the case. This study involved showing glare illusions to subjects in a variety of different colors, and concluded that a blue glare illusion was perceived to be the brightest among all the colors and that subjects' pupils constricted significantly in relation to this perception. The results of this study were published in the Dutch journal, Acta Psychologica on July 6.

PhD candidate, Yuta Suzuki (left), his supervisor, Professor Shigeki Nakauchi (2nd from left) and co-researchers

The research team hypothesized that the blue glare illusion would be perceived as the brightest because the color blue is most associated with the sky and sunlight typically appears to have a gradient of luminance. In other words, the team surmised that the human visual system often relies on ecologically-based predictions to interpret visual input. The results of this study show that the blue glare illusion was evaluated to be brighter than any other color and that viewing this illusion resulted in significant pupil contraction. This effect is thought to be unique to glare illusions, as it was not observed for visual stimuli without any illusory glare effects.

Lead author and Ph.D. course student, Yuta Suzuki explains "The pupillary light reflex, in which the pupil constricts and dilates, follows a very concise route in neural processing. The same goes for the pupil responses we saw when subjects viewed the blue glare illusion in this study – the difference of larger pupil constriction among colors occurred with the pupillary light reflex. This may indicate that we have evolved to develop a faster pupillary reaction for illusions in specific colors. We also saw a correlation between pupil contraction and individual brightness perception. We hope to be able to use the pupillary light reflex as a simple tool for evaluating individual differences in brightness perception."

Assistant Professor Tetsuto Minami, who lead the research team, says that "Subjective brightness perception is an individual phenomenon that cannot be verified by others. That is, we could only rely on peoples' own reported brightness perception. In this study, we saw a correlation between brightness perception and pupil contraction, and this is a new development that can be used as an index for evaluating objective brightness perception."

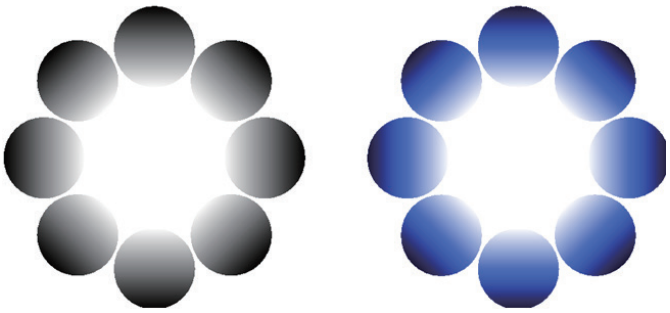
Professor Shigeki Nakauchi, the Project Leader, mentions that "The pupillary light reflex has drawn attention as a way to investigate a person's mental state through non-contact measurement. Work involving the pupillary light reflex will create innovative, fundamental technologies that can achieve rapid progress in communication between humans as well as between humans and robots."

This work was supported by JSPS KAKENHI Grant Numbers JP17H06292 (Challenging Research (Pioneering)), JP17H01807 (for Scientific Research) and JP18J11571 (for JSPS Fellows) from the Japan Society for the Promotion of Science (JSPS). The lead author Yuta Suzuki also received assistance from the Program for Leading Graduate Schools run by the Japan Society for the Promotion of Science.

Reference

Y. Suzuki, T. Minami, B. Laeng, and S. Nakauchi, "Colorful glares: Effects of colors on brightness illusions measured with pupillometry," Acta Psychologica, vol. 198, p. 102882, Jul. 2019.

http://dx.doi.org/10.1016/j.actpsy.2019.102882



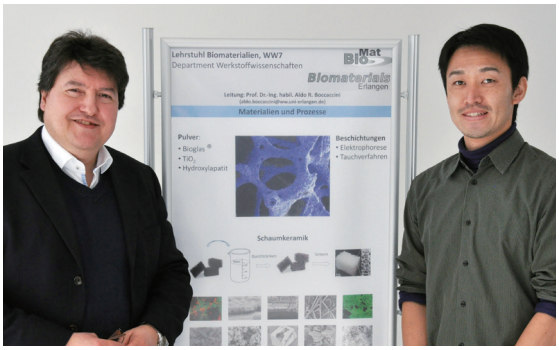
Black and blue glare illusions: Glare illusion is an optical illusion that has a luminance gradient towards the center and is perceived as brighter by the gradient.

Affordable multiferroic material

An important first step towards a wide-range of practical applications of advanced materials

By Go Kawamura

An international research team led by Toyohashi University of Technology, with the collaboration of the Japan Fine Ceramics Center, the National Institute of Technology Ibaraki College, the International Iberian nanotechnology Laboratory, Chang'an university and The University of Erlangen-Nuremberg, has developed a novel liquid process for fabrication of an affordable multiferroic nanocomposite film. The multiferroic material obtained by the novel process has a strong correlation between its electric and the magnetic properties which makes it a promising material for various future applications such as low-power-consumption large-volume memory, spatial light modulators and unique sensors, etc.



Associate Prof. Kawamura (right) and his co-researcher, Prof. Boccaccini

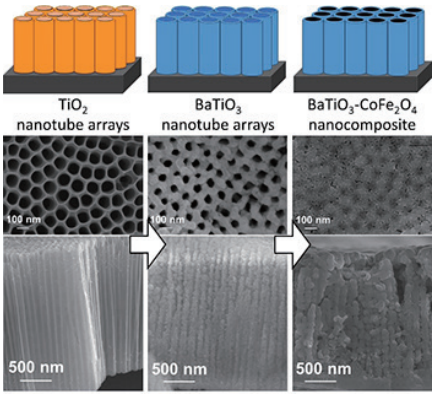
Multiferroic materials combine electrical (ferroelectric) and magnetic (ferromagnetic) properties and have a strong correlation between these properties, i.e. they exhibit a magnetoelectric effect. Their development is expected to realize more versatile and higher performance next-generation electrical and magnetic devices. In recent years, several methods of production of multiferroic films exhibiting large magnetoelectric properties have been reported. However, these processes require large and extraordinarily expensive vacuum devices, making them impractical for fabricating materials with a large surface area in particular. As a result, multiferroic materials have only been used in a very limited range of applications.

The new material with advanced multiferroic properties developed by the research team, however, was created by combining several liquid-phase methods that are relatively inexpensive and simple.

The lead author, Associate Professor Go Kawamura of Toyohashi University of Technology explained, "In order to fabricate a material that exhibits advanced multiferroic properties, it is necessary to combine ferroelectric and ferromagnetic materials appropriately and periodically on the nanometer scale. In the past, nanopillar array structures were fabricated in a self-organized manner using gas-phase methods, and a large magnetoelectric effect was observed in such materials. However, the gas-phase methods required the use of large and expensive equipment, and it was practically impossible to increase the area of the sample. Therefore, we worked on the fabrication of nanopillar array-like composite films using only affordable and simple liquid-phase methods. We were able to demonstrate that the multiferroic composite film we created has a local epitaxial relationship at the interface between the ferroelectric and the ferromagnetic materials, thereby producing a large magnetoelectric effect. Compared to conventional gas-phase processes, multiferroic composite films can be produced at a much lower cost and can be used for larger areas."

This study required an interdisciplinary approach since it required expertise across a variety of specialties. Therefore, the research team collaborated with specialists in dielectric materials and magnetic materials, specialists in observation of nanostructures using electron microscopes, and specialists in liquid-phase synthesis, among others, from various institutions in Japan and overseas. The novel process was developed by combining these advanced specialties.

The research team believes that greater precision in the creation of controlled nanostructures can lead to a further improvement of the magnetoelectric effect, and will continue to optimize the process. Ultimately, the team plans to produce large area materials, which is also a feature of the process that was developed, and apply them to a spatial light modulator to develop applications such as spatial displays that can build huge three-dimensional images.



Images of the multiferroic nanocomposite film fabricated by the developed process.

This work was financially supported by the Program for Fostering Globally Talented Researchers (R2802), JSPS. TG, YN, and MI acknowledge JSPS KAKENHI [Grant Nos. 17K19029, 16H04329, and 26220902]. TG acknowledges JST PRESTO [Grant No. JPMJPR1524]. FLD acknowledges the N2020; Nanotechnology based functional solutions (NORTE-45-2015-02).

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Go Kawamura, Kentaro Oura, Wai Kian Tan, Taichi Goto, Yuichi Nakamura, Daisaku Yokoe, Francis Leonard Deepak, Khalil El Hajraoui, Xing Wei, Mitsuteru Inoue, Hiroyuki Muto, Kazuhiro Yamaguchi, Aldo R. Boccaccini and Atsunori Matsuda (2019). Nanotube array-based barium titanate–cobalt ferrite composite film for affordable magnetoelectric multiferroics. Journal of Materials Chemistry C, 7, 10066-10072. DOI: 10.1039/C9TC02442E

http://dx.doi.org/10.1039/C9TC02442E

Making Cut Flowers Last Longer

Development of plasma nutrient water production system and plasma gas freshness preservation system

By Hirofumi Takikawa

Professor Hirofumi Takikawa and Assistant Professor Toru Harigai at the Electrical and Electronic Information Engineering Department and Associate Professor Takahiro Yamauchi at the Research Center for Agrotechnology and Biotechnology, a research group of Toyohashi University of Technology, have been working on the development of technology that can make cut flowers last longer. In order to realise a practical implementation of the developed technology, the research team collaborated with Sinfonia Technology Co., Ltd. in Toyohashi, to develop a plasma nutrient water production system and a plasma gas freshness preservation system.

The flower industry faces several issues such as strengthening brands, saving cost and energy in production, preserving freshness and improving vase life, and improving resistance to diseases. Among these, preserving freshness and improving vase life are expected not only to make products more appealing, but also to open up new opportunities for distribution such as overseas exports. In recent years, efforts have been underway to guarantee a long vase life.

Against this background, Toyohashi University of Technology has developed a technology that uses discharge plasma to sterilize tap water and at the same time produce plasma nutrient water containing nitrogen oxides, which act as nutrients for plants. A patented material was used for the discharge electrode, a system of sensors that constantly measures the concentration of nitrogen oxides (nitrate ions and nitrite ions) in the production line was developed, and a patent was applied for. Sinfonia Technology Co., Ltd. has now produced a plasma nutrient water production system incorporating these technologies.

The system can produce 6 liters of high-concentration plasma nutrient water in 10 hours. In actual use, this is diluted to 50% concentration. Power consumption is low at about 120W. The company has also developed a new system (plasma gas freshness preservation system) that irradiates plasma gas containing ozone when unloading products before shipping. In terms of performance, the effect of extending the vase life of roses was confirmed in joint research conducted with JA Aichi Minami.

In addition, the research group is also promoting the development of optical environment measurement technology using solar cells to contribute to the increased use of IoT in the agricultural field. The group has provided technology to Sinfonia Technology Co., Ltd. and developed a photon flux density measuring device (band-spectral quantum meter) with a resolution of 100 nm. With this device, the growth environment can be easily confirmed.

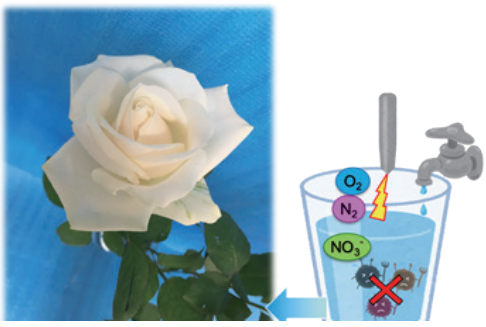


Fig.1 Concept of the production process of plasma nutrient water

Fig.2 Plasma nutrient water production system

次世代型高容量リチウムイオン電池の実現に向けて

リン化錫・炭素複合膜電極のバインダレス形成による長寿命化

稲田　亮史

豊橋技術科学大学の研究グループは、エアロゾル・デポジション（AD）法を用いてバインダ（結着材）を用いず、リン化錫（Sn_4P_3）/カーボン（C）複合膜を金属基板上に形成することに成功しました。原料であるSn_4P_3/C粒子が基板に衝突した際の衝撃により変形・固化することにより、複合膜が形成できたと考えられます。カーボン複合化とリチウム脱離反応時の電圧の制御を組み合わせることで、充放電サイクル特性が向上することを確認しました。本成果は、次世代型高容量リチウムイオン電池の実現に貢献すると考えられます。

リチウムイオン電池は、携帯用小型電子機器の電源として広く使用されており、最近では電気自動車、プラグインハイブリッド電気自動車、および定置型蓄電システム等の中・大型電源としての用途展開が加速しています。大容量な次世代型リチウムイオン電池の実現には、容量の高い負極材料の開発が望まれます。シリコンや錫は、リチウムとの合金化反応を通じて、現行の黒鉛負極（理論容量：372mAh/g）よりもはるかに大きな理論容量を示すため精力的に研究されています。しかしながら、合金化（充電）・脱合金化（放電）時の体積変化が大きく、サイクル安定性が低いことが課題となっています。

リン化錫Sn_4P_3（理論容量：1255mAh/g）は、リチウム基準で約0.5Vの電位で作動する高容量合金系負極材料の一つです。ナノサイズ化したSn_4P_3をカーボン（C）と複合化することで、そのサイクル安定性が向上することが既に確認されています。一般的にリチウムイオン電池の電極は、充放電を担う材料（活物質）と導電助剤、バインダ（結着材）および溶剤を混合してスラリーを作製し、これを金属箔上に塗布・乾燥する工程で作製されます。Sn_4P_3/C複合粒子を活物質とした先行研究では、サイクル安定性向上のため多量の導電助剤・バインダを混合しており、最終的な電極内での活物質の充填率（重量）は60～70%となり、電極総重量あたりの容量値が低下するという課題があります。

豊橋技術科学大学電気・電子情報工学系の稲田亮史准教授と森高冬毅（2019年3月博士前期課程修了）の研究グループは、エアロゾル・デポジション（AD）法を用いてバインダ（結着材）を用いず、Sn_4P_3/C複合膜を金属基板上に形成することに成功しました。Sn_4P_3粒子にカーボン材料（アセチレンブラック）を簡便なボールミル処理によって複合化し、衝撃固化を介して導電助剤やバインダを加えることなく、金属基板上に固化させました。本手法により、電極内での活物質の充填率は80%以上に調整しました。カーボンの複合化および放電（脱合金化）電位の制御により、充放電サイクル時の電極構造の変化が抑制され、充放電サイクル安定性の顕著な向上を確認しました。結果として、100サイクル後で黒鉛負極の2倍に相当する730mAh/g、200サイクル後で500mAh/g、400サイクル後で400mAh/gの可逆容量を保持することができました。

筆頭著者の森高冬毅（2019年3月本学博士前期課程修了）は、「成膜条件の検討に苦労しましたが、Sn_4P_3/C複合膜電極のサイクル安定性向上に向けた有益な知見が得られました。複合化したカーボンは、Sn_4P_3の大きな体積変化によって誘発される電極崩壊を抑制すると共に、電極内で変形・微粒化した活物質粒子間の電気伝導パスを担っていると考えます」と説明しています。

また、指導教員である稲田亮史准教授は、「電極総量あたりの容量値を高める上で本プロセスは有効な手段であり、複合膜の作製に使用するSn_4P_3/C複合粒子のサイズやカーボンの種類・量の調整によって更なる性能改善が達成可能と考えています。電極の厚膜化と併せて、更なる性能改善に向けた検討を進めています」と、述べています。

本研究の成果は、次世代型高容量リチウムイオン電池の実現に貢献するものと考えます。また、Sn_4P_3はリチウムのみならず資源的制約の少ないナトリウムについても合金化・脱合金化反応を示すため、リチウムイオン電池よりも低コスト化が可能なナトリウムイオン電池用電極への応用も期待できます。

本研究の一部は日本学術振興会（JSPS）科学研究費助成事業（課題番号16K06218および16KK0127）の支援の下で実施されたものです。

様々な色のグレア錯視に対する瞳孔反応

青いグレア錯視は最も明るく知覚され、より大きな瞳孔縮小を引き起こす

鈴木　雄太

豊橋技術科学大学　情報・知能工学系とオスロ大学の研究チームは、ヒトが明るさの錯視（グレア錯視）を見ているときの瞳孔（眼球にある、いわゆる黒目と呼ばれる部分）の大きさを計測しました。瞳孔は、暗い場所では散大し（散瞳）、明るい場所では縮小して（縮瞳）、目に入る光を調節する働きを持ちます。一方で、ヒトが錯覚で明るく感じたときにも同様に縮瞳することが知られています。本研究は、様々な色相のグレア錯視において、青色の錯視が最も明るく知覚され、さらに大きな瞳孔の縮小が知覚と関連して生じることを見出しました。本研究成果はオランダの科学誌 Acta Psychologica に7月6日付けで掲載されました。

研究チームは、最も空に関連のある色は青で、太陽の光は輝度の勾配を持つように見えるので、青いグレア錯視は最も明るく知覚されるのではないかと考えました。つまり、視覚システムにおいて、生物学的な背景を持つ予測が入力を理解するために重要であると考えたのです。研究の結果、青いグレア錯視は他の色と比べて明るいと評価され、またその錯視を見ているときには大きな瞳孔縮小が見られました。これは錯視の効果を無くした視覚刺激に対しては観測されなかったので、グレア錯視に特異的な効果であると考えられます。

「瞳孔が縮瞳・散瞳するような対光反射の反応は、脳処理において非常に簡潔な経路をたどっています。本研究で得られた青色グレア錯視に対する瞳孔反応も同様に、比較的早い反応時間で、他の色のグレア錯視よりも大きな縮小を示していました。したがって、そういった色依存の錯視に対する早い瞳孔反応は、進化の過程で我々は獲得してきたことを示すものかもしれません。また、瞳孔の縮瞳と個人の明るさ知覚には相関関係が見られました。このことから、明るさ知覚における個人差を評価する簡単なツールとして、瞳孔反応が利用できるのではないかと考えています。」と筆頭著者である博士後期課程の鈴木雄太は説明します。

研究チームのリーダーである南哲人准教授は「主観的な明るさ知覚は、本人にしかわからないといった、いわゆる一人称視点での知覚報告に頼るしかありませんでした。今回、明るさ知覚と瞳孔縮小との相関が見られたことから、客観的な明るさ知覚を評価する指標として新たな展開が期待できます。」と説明します。

プロジェクトリーダーの中内茂樹教授は「瞳孔反応は非接触計測によって心的状態を探るための有力な手がかりとして注目されており、ヒト同士のコミュニケーション、ヒトとロボットのコミュニケーションを飛躍的に発展させるイノベーティブな基盤技術となるでしょう」とコメントしています。

本研究は、文部科学省・日本学術振興会科学研究費挑戦的研究（開拓）（17H06292）、基盤研究B（17H01807）、特別研究員奨励費（18J11571）の助成によって実施されたものです。また、筆頭著者の鈴木は文部科学省・日本学術振興会の実施する博士課程教育リーディングプログラムの支援を受けました。

マルチフェロイック材料を安価・簡便に作る

最先端材料の汎用化に向けた第一歩

河村　剛

豊橋技術科学大学は、(一般財団法人)ファインセラミックスセンター、茨城工業高等専門学校、ポルトガルの国際イベリアナノテクノロジー研究所、中国の長安大学、ドイツのエアランゲン－ニュルンベルグ大学との共同研究により、高度なマルチフェロイック特性を示すナノ複合膜を、安価で簡便に作製できる液相プロセスを開発しました。このプロセスで得られるマルチフェロイック材料は、電気的特性と磁気的特性の間に強い相関をもつため、将来的に低消費電力・大容量のメモリデバイスや空間光変調器、様々なセンサ等への応用が期待されます。

電気的な特性(強誘電性)と磁気的な特性(強磁性)を併せもち、かつそれらの特性間に強い相関をもつ(電気磁気効果を示す)マルチフェロイック材料は、より多機能で高性能な次世代電気・磁気デバイスの実現に向けて開発が期待されています。近年、大きな電気磁気特性を示すマルチフェロイック膜の作製例がいくつか報告されましたが、それらのプロセスでは、非常に大型で高額な真空装置などが必要であり、特に大面積の材料を作製することは現実的ではありませんでした。そのため、マルチフェロイック材料の応用検討はごく限られた範囲に限定されていました。

そこで、研究チームは比較的安価で簡便ないくつかの液相法を組み合わせることで、高度なマルチフェロイック特性を示す材料を作製するプロセスを開発しました。

「高度なマルチフェロイック特性を示す材料を作製するには、強誘電体と強磁性体をナノメートルスケールで適切にかつ周期的に複合化する必要があります。従来は、気相法によって、自己組織的にナノピラーアレイ構造などを作製し、その材料において大きな電気磁気効果が観測されていました。しかし、採用されていた気相法では、大型で高価な設備の使用が必須であり、また試料の大面積化が現実的に不可能でした。そこで、安価で簡便な液相法のみを駆使してナノピラーアレイライクな複合膜の作製に取り組みました。

今回開発したプロセスで得られるマルチフェロイック複合膜では、強誘電体と強磁性体の界面において、局所的にエピタキシャルな関係を有していることが明らかとなり、それによって大きな電気磁気効果を発現することがわかりました。従来の気相プロセスに比べて非常に安価にマルチフェロイック複合膜を作製することができ、かつ大面積化にも対応可能です。」と筆頭著者である豊橋技術科学大学の河村剛准教授は説明します。

この研究は、様々な専門性を必要とする学際的なものでした。そこで、国内外の様々な機関に在籍している誘電材料や磁性材料の専門家、電子顕微鏡でのナノ構造観察の専門家、液相合成法の専門家などと協力し、それぞれの高度な専門性を融合することで、これまでにないプロセスの開発につながりました。

研究チームは、制御されたナノ構造をより精密に作り込むことで、電気磁気効果をさらに改善できると考えており、引き続きプロセスの最適化に取り組んでいます。最終的には、開発したプロセスの特徴でもある材料の大面積化を行い、空間光変調器へ応用することで、巨大な3次元像を構築できる空間ディスプレイなどへの展開を考えています。

切り花を長持ちさせる

プラズマ栄養水製造装置およびプラズマガス鮮度維持処理装置の開発

滝川 浩史

豊橋技術科学大学電気・電子情報工学系の滝川浩史教授・針谷達助教、先端農業・バイオリサーチセンターの山内高弘特任准教授らのグループは、切り花を長持ちさせる技術の開発に取り組み、シンフォニアテクノロジー株式会社と共同でプラズマ栄養水製造装置およびプラズマガス鮮度維持処理装置を開発しました。

花き産業においては、ブランド力強化、省コスト・省エネ生産、鮮度維持・日持ち性向上、耐病性向上、などの課題を抱えています。このなかで、鮮度維持・日持ち性向上については、商品力アップのみならず、海外輸出などの流通改革をもたらすものとして期待されています。近年では、日持ちを保証する取り組みも始まってきています。

このような中、豊橋技術科学大学は放電プラズマを用いて、水道水を殺菌すると同時に、植物の栄養分となる窒素酸化物を含ませたプラズマ栄養水を製造する技術を開発しました。放電電極には特許取得済みの材料を用い、また、製造ラインにおいて窒素酸化物(硝酸イオンおよび亜硝酸イオン)の濃度を常時計測するセンサリングシステムを開発し、特許出願しました。これらの技術を組み込んだプラズマ栄養水製造装置をシンフォニアテクノロジー株式会社が装置化しました。

同装置は、6リットルの高濃度プラズマ栄養水を10時間で製造できます。実際の利用の際には2倍に薄めます。消費電力は約120Wと低電力です。また、出荷前の水揚げ時にオゾンを含むプラズマガスを照射する装置(プラズマガス鮮度維持処理装置)も開発しました。これらの性能について、JA愛知みなみとの共同研究において、バラを対象として日持ち延長効果を確認しました。

更に、同研究グループは、農業分野のIoT活用拡大に寄与するため、太陽電池を使った光環境計測技術の開発も推進しており、今回シンフォニアテクノロジー株式会社に技術提供し、100nm刻みの光量子束密度計測装置(帯域分光式光量子計)を開発しました。この装置を用いれば、手軽に育成環境を確認できます。

Pick Up

Industry-Academia Collaboration Bridging Accelerating TUT Research Seeds into Commercial Products

"Knowledge Hub AICHI" priority research project is an important program, with annual funding of 1 billion yen, aimed at creating and developing industries in Aichi Prefecture, where Toyohashi University of Technology (TUT) is located.
TUT completed the research and development stages, Phases Ⅰ (2011-2015) and Ⅱ (2016-2018), before launching Phase Ⅲ in 2019. For this phase, 14 TUT researchers have been working on research and development projects in collaboration with private companies. These projects have been organized according to five research themes within the three key fields of ***automobiles, smart factories*** and ***basic manufacturing technology.***

"Knowledge Base of AICHI" Strategic Research Project - Phase III (2019 - 2021)
Projects lead by Toyohashi University of Technology

Near Future Automotive Technology

Wireless power transmission system for compact vehicles (Prof. Takashi Ohira)

- Development of unmanned automated wireless power transfer system for battery-less compact EV

Advanced traffic safety management system (Assistant Prof. Kojiro Matsuo)

- Development of traffic safety management system using big data collected by advanced probes

Advanced AI / IoT / Big Data Utilization Technology

Business deployment of natural language processing technology by field adaptation (Prof. Hitoshi Isahara)

- Development of machine translation technology and chat bot system adaptable to each company's technical terms

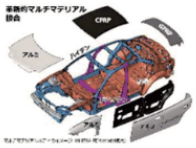
Robot greenhouse using agricultural big data (Prof. Jun Miura)

- Construction of big data on crop growth and disease corresponding to environmental factors and development of support system of using its analysis

Innovative Manufacturing Technology

Lightweight and high-performance mobility by innovative multi-material bonding (Prof. Toshiaki Yasui)

- Development of joining technology of dissimilar metals and dissimilar materials for weight reduction of EV bodies



One of TUT's main missions is to promote social implementation of its research results. In accordance with this goal, we established the Research Institute for Technology Science and Innovation in 2016, to promote R & D and industry-academia collaboration.

As for funding, TUT directly funds its own "Collaborative Innovation Research Project" with support from external funds. In addition, we are active participants in the"Knowledge Hub Aichi" priority research project which is funded by Aichi Prefecture.

During Phase Ⅰ, the "Collaborative Innovation Research Project" (2016-2018), TUT worked on achieving social implementation of a number of research themes. For Phase Ⅱ, 13 themes were chosen to receive for 3 years of support. Phase Ⅲ provides large-scale matching funds of 10 million yen for some projects.

TUT Research
e-Newsletter from Toyohashi University of Technology
https://www.tut.ac.jp/english/newsletter/

Toyohashi University of Technology

The Toyohashi University of Technology (TUT) is one of Japan's most innovative and dynamic science and technology based academic institutes. TUT Research is published to update readers on research at the university.

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