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FEATURE STORY

How organic chemistry can contribute to society

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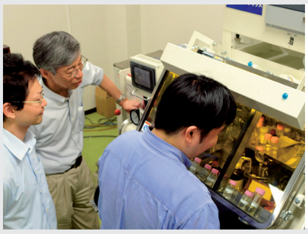
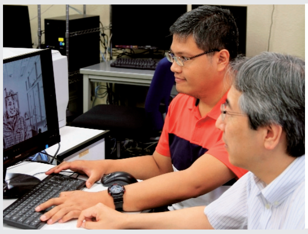
Research Highlights



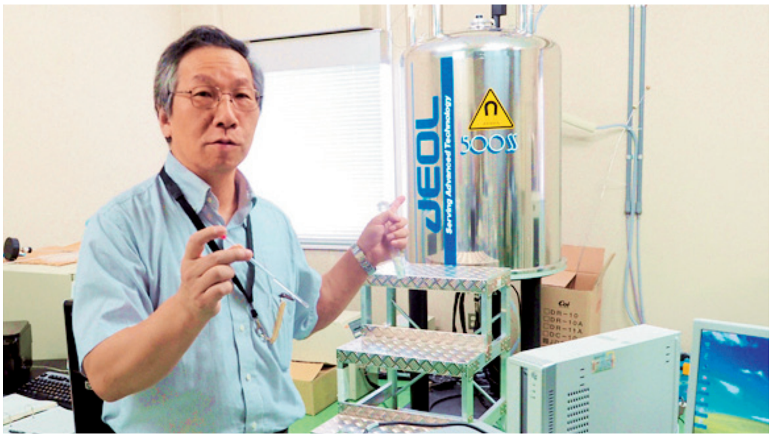


Pick Up

How organic chemistry can contribute to society

Applications of recent advances in research, such as in drug discovery and pesticide detection

Seiji Iwasa



Professor Iwasa's research involves studying and synthesizing organic compounds and devising ways to use those compounds in the fields of medicine and health, such as molecular sensors. Specifically, he extracts various organic compounds produced in nature and determines their molecular structures, and synthesizes useful biologically active compounds by freely manipulating the bonds of organic compounds. As synthesizing useful organic compounds with complicated molecular structures in large batches quickly can be helpful in areas such as drug discovery and food safety, this high-profile field of research has been widening its scope of applications in recent years.

Interview and report by Madoka Tainaka

Determining the structures of natural products and achieving total synthesis

Professor Seiji Iwasa became interested in the world of organic compounds as a result of his fascination with the miraculous properties of medicinal herbs and other natural products. After that point, guided by his curiosity, he worked toward becoming a researcher in natural products chemistry.

Professor Iwasa says, "Just as Ninjas once used aconite poison as a weapon by wiping it on the tips of their Shuriken, there are many surprising natural products in this world that can take a person's life even when used in tiny quantities. However, aconite also has beneficial cardiotonic and analgesic effects, and thus has long been used as a medicine as well. That shows that even poison can be a medicine if used properly. Nevertheless, in order to use such products effectively, we need to understand their structures and functions. It is the mission of [A1]:Organic sounds better, but I don't know if 'Natural Product Chemist' is an official name to make these products useful by reproducing them synthetically, a process which is called 'total synthesis'."

At that time, Professor Iwasa was working on the total synthesis of strychnine, an extremely toxic alkaloid. The molecular structure of strychnine was uncovered in the mid-20th century after a century of effort. After that discovery, R.B. Woodward et al. succeeded in completing the synthesis of strychnine in 37 steps. Professor Iwasa and his team successfully shortened the process by more than half, to just 12 steps. This was in 1994.

"The method we used is called retrosynthetic analysis, and it involves exploring how to synthesize a substance by breaking down the synthetic process step-by-step while analyzing the molecular structure. This method allowed us to more easily synthesize strychnine. This field deals with molecules, which have a three-dimensional form. Because of this, it requires big leaps in topological thinking and mathematical sense. That is why this research is so thrilling to me," says Professor Iwasa.

Catalytic asymmetric reactions: A promising tool for drug discovery

In order to seriously investigate the methodology for further shortening and simplifying the process of total synthesis, Professor Iwasa is currently focusing his efforts on the development of catalytic asymmetric synthesis. Asymmetric synthesis is a method of synthesizing optical isomers, which has come to be used in the development of most drugs in recent years.

Professor Iwasa explains the concept. "An optical isomer is a compound that cannot be superimposed on its opposite compound, like a human's right and left hands. In essence, it is a mirror image of a substance. In the case of most optical isomers, the right-handed one has a therapeutic effect, whereas the left-handed one is toxic. Even though the substances look the same, they have completely opposite physiological properties."

One well known example of this is thalidomide. Thalidomide, a drug developed as a hypnotic and sedative, caused a global tragedy in 1957 due to the toxicity of one of its isomers, which caused the children of mothers who took the drug while pregnant to be born with limb malformations. When normal methods of synthesis are used, both the right-handed and left-handed optical isomer are produced at the same time. Essentially, this tragedy occurred because both isomers were present in the drug. Therefore, in order to safely use an optical isomer as a drug, it is necessary to skillfully produce just the isomer with the useful properties. This can be done by asymmetric synthesis.

Professor Iwasa developed a method for performing these reactions using an unstable carbene intermediate and an organometallic complex. This acts as a highly active catalyst because of the electrical properties of the metal. When this is combined with the asymmetric environment of the organic ligand, just one optical isomer of the substance is produced selectively. This is what is called a 'catalytic asymmetric reaction'. Actually, the first person to use a metallic complex as a catalyst in asymmetric reactions was Dr. Ryoji Noyori, who won the Nobel Prize in Chemistry in 2001.

"To give an analogy, an asymmetric reaction is like setting out a glove that will only fit the left hand, so that it will only recognize the left hand. For example, a substance called chrysanthemic acid that is used in mosquito coils is also an optical isomer, and is efficiently synthesized through an asymmetric reaction catalyzed by metal. The trick is that using a complex formed from an organic metal with high electron density and a highly configurable ligand as a catalyst makes it easy to control the reaction."

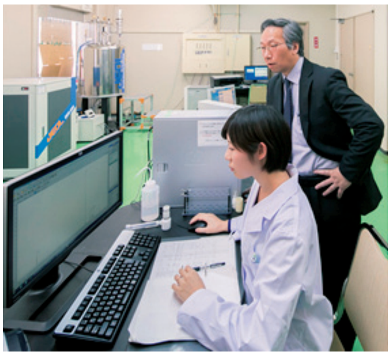
In recent years, Professor Iwasa has also incorporated computer science into his research. He has started a project to explore reaction mechanisms regulated at different intensities by analyzing reaction mechanisms through simulations. He has also branched out to working on making catalysts non-toxic after use in chemical reactions.

"I believe that my job is to create new fields within organic chemistry and to keep expanding their reach."

A wide scope of work ranging from molecular sensors to development of drug substances

One of Professor Iwasa's achievements, that exemplifies the wide-ranging scope of his research, is his project to develop a kit for testing for residual pesticides using immunochromatography. He worked on this project as part of the Food Safety Technology Project, one of the core research projects of Knowledge Hub Aichi, which is run by the Aichi prefectural government. It involves the simple detection of residual pesticides by employing antibody reactions, which are part of organisms' immune systems, a field of study quite different from total synthesis.

"Testing devices have conventionally been large and expensive, require trained specialists to operate, and take a long time to run tests. Our goal for this project was to develop a low-cost system that is convenient and fast to use in places such as manufacturing plants and overseas. That is why we turned our attention to organismal immune systems."



However, pesticide molecules are too small to elicit an immune response without alteration. Therefore, Professor Iwasa made the pesticide molecules bigger by attaching a massive protein extracted from shellfish, and experimented by injecting those molecules into mice. The mice recognized the molecules as foreign bodies and produced countless antibodies. Antibodies against the pesticide are sorted out from amongst those antibodies and fused to detoxified cancer cells to promote proliferation. Essentially, Professor Iwasa made antibodies against pesticides proliferate endlessly by exploiting the properties of cancer cells.

"When antibodies produced in this way are planted onto gold colloid, which acts as an antibody label, and a solution containing the pesticide is run across it, an immune response is elicited. This kit determines the concentration of pesticide by measuring absorbance," Professor Iwasa explains. He has created two different kits; a kit like

a pregnancy test for simple visual confirmation, and a quantitative kit that uses optical equipment, so that they can be used for different purposes. He says that he is now working on how to make these into products.

In addition to this work, he has developed a method for extracting a useful substance from Melaleuca leaves in a joint project with Ho Chi Minh City University of Technology in Vietnam. This substance is already being used as a drug substance. Professor Iwasa says that while conducting this research, he traveled by canoe into Vietnamese forests with thick-growing Melaleuca groves.

"Curiosity has always been what has driven my research. As long as I have curiosity, I can go anywhere. Even still, I felt a bit scared in the forest in Vietnam." It seems that Professor Iwasa's curiosity still has no limit.

[Reporter's Note]

After finishing his degree at Chiba University, young Professor Iwasa wrote letters to research institutions all over the world telling them of his desire to pursue the study of organic chemistry. He got his first response from the University of Ohio, despite having no connections there. He then went to the United States, where he achieved several research accomplishments, including the synthesis of strychnine, and later got an offer from the University of Chicago. This moment made him feel how open-minded Americans are and how strong their researcher network is.

In order to return the favor, Professor Iwasa is making an active effort to recruit international students. Students from eight different countries, including China, Mongolia, Laos, and Malaysia, are currently working with him in his laboratory.

"Learning about the world like that has reminded me of what is good about Japan. I want to bring good aspects of Japan such as its advanced technological capabilities, strong morality, and respect for the environment to the rest of the world. To that end, I am currently engaged in Japanese language education in Asia as well," says Professor Iwasa.

His curiosity is extending beyond his research to education and the environment as well.

創薬や農薬の検知など、有機化学の先端研究で社会に貢献する

岩佐精二教授の研究は、自然が生み出すさまざまな有機物質を抽出し、分子構造を解き明したり、また有機化合物の結合を自在に操ることで、有用な生理活性物質を合成したり、分子センサーとして応用するなどして、医療や健康に役立てるというもの。複雑な構造を持つ有用な有機化合物を大量かつスピーディに合成できれば、創薬や食の安全などに役立てられるとして、近年、その応用範囲を広げつつある注目の研究分野である。

天然物の構造を明らかにし、全合成する

岩佐精二教授が有機化合物の世界に興味を抱いたのは、薬草などが持つ驚異の力に魅せられたのがきっかけだった。

以来、好奇心に導かれ、「天然物化学」の研究者の道へ進んだのだという。「かつて忍者が、トリカブトの毒を手裏剣に塗って武器として利用していたように、世の中にはほんのわずかな量でも命を奪うような驚くべき天然物があります。一方でトリカブトには強心作用や鎮静作用があるとして、古くから薬としても用いられてきたように、毒もうまく使えば薬になる。ただ、それらを有効に使うためには、その構造と機能を明らかにする必要があります。さらにそれらを人工的につくり出す、すなわち全合成をして役立てるのが天然物化学の使命です」と岩佐教授は語る。

そうした中、かつて岩佐教授が手がけたのが、ストリキニーネと呼ばれるアルカロイド系の毒性が非常に強い物質の全合成だった。ストリキニーネの分子構造は20世紀半ばに1世紀かけて明らかにされたもので、その後、Woodward,R.Bらが37ステップによる全合成に成功。それを岩佐教授らは半分以下の12ステップに縮めることに成功したのである。1994年のことだ。

「逆合成解析と言いますが、分子構造を分解しつつ、ステップごとのパーツに分けて合成の仕方を探るのです。これにより、より簡単にストリキニーネを合成できるようになりました。この分野は、分子という三次元の形を扱うことから、ある意味、位相幾何学的な発想の飛躍と数学的なセンスが必要であり、そこに研究の醍醐味があります」と岩佐教授は言う。

創薬で期待される「触媒的不斉反応」

さらに、全合成をより短く、簡便にできないか ― その方法論を突き詰めるために、現在、岩佐教授が注力するのが「触媒的不斉反応の開発」である。不斉反応とは、近年、ほとんどの医薬品に利用されている光学異性体を合成するための手法の一つだという。

「光学異性体というのは、人間の右手と左手のように、重ね合わすことができない化合物のこと。つまり、鏡写しの関係にある物質です。光学異性体の多くは、右手系は薬として有用でも、左手系は毒性を持つといった具合に、同じように見えても、その生理活性はまったく異なります」と岩佐教授は説明する。

その一例として有名なのがサリドマイドだ。1957年に睡眠鎮静薬として開発されたサリドマイドの片方に毒性があったため、この薬を服用した妊婦から生まれた胎児に四肢欠損が生じるという、世界規模の悲劇が起こった。通常の合成法を用いる限り、右手系・左手系の光学異性体は同時に生成されてしまう。つまり、両方が含まれていたことに原因があった。したがって、光学異性体を薬として安全に活用するためには、有用な機能を持つ片方だけをうまくつくり分けなければならないのだ。その片方だけをつくり分けるのが不斉反応である。

その際、岩佐教授は不安定なカルベン中間体と有機金属錯体を利用し、金属が持つ電子的な性質を利用して活性の高い触媒として用い、有機配位子の不斉環境と組み合わせることで、選択的に片方の物質だけをつくる手法を開発した。これがすなわち、「触媒的不斉反応」だ。じつは、不斉反応の触媒として金属錯体を最初に採用したのは、2001年にノーベル化学賞を受賞した野依良治氏らである。

「たとえるなら、不斉反応というのは左手だけにフィットするようなグローブを用意してあげて、左手だけを認識させるというもの。たとえば、蚊取線香に使用される菊酸という物質も光学異性体で、金属を触媒とした不斉反応により効率よく合成されています。電子密度の高い有機金属と微調整可能な配位子からなる錯体を触媒として使うことで、反応がコントロールしやすいところがミソなんですね」

岩佐教授は近年、計算機科学を取り入れて、シミュレーションで反応機構を解析することにより、さまざまな高度に制御された反応機構を探る取り組みも始めている。さらに化学反応後の触媒の無害化にも手を広げる。

「有機化学の新たな領域を創出し、射程距離を広げていくのが私の仕事だと思っています」

分子センサーや医薬品の原料開発まで幅広く

その岩佐教授の幅広い研究を象徴する成果の一つが、「イムノクロマト法による残留農薬検査キットの開発」である。これは、愛知県が推進する「知の拠点あいち」重点研究プロジェクトの一つ、食の安心・安全技術プロジェクトの一環として取り組んだ研究で、残留農薬の検知を、生物の免疫システムである抗体反応を活用して簡便に調べるというもの。全合成とはかなり違う分野の研究だ。

「従来の、検査機器は大型で高価なうえ、熟練した専門家が必要で検査に時間を要するものが多かったのですが、ここでは生産現場や海外などで簡便に素早く使える安価なシステムを目指しました。そこで目をつけたのが、生物の免疫システムです」

しかし、農薬の分子は、そのままでは小さすぎて免疫応答を起こさない。そこで、農薬に貝から抽出した巨大なたんぱくをつけて大きな分子にし、これをマウスに投与した。するとマウスはこれを異物だと認識して、無数の抗体をつくり出す。その中から農薬に反応する抗体だけを取り出し、さらにがん細胞を無毒化した細胞と融合させて、増殖させたのだという。つまり、農薬に反応する抗体を、がん細胞の性質を利用して無限に増殖させたわけだ。

「こうして生産した抗体を、抗体標識となる金コロイドに植え付け、その上に農薬が含まれた液体を流すと免疫反応が起こります。その吸光度を測ることで農薬の濃度がわかるというしくみです」と、岩佐教授は説明する。

キットは、妊娠検査キットのように目視で簡単に確認できるものと光学機器を使って定量的に測れるものを用意し、用途に応じて使い分けできるようにした。現在、製品化に向けて検討しているところだという。

そのほかにも、ベトナム・ホーチミン市工科大学と共同で、ユーカリの葉から有用な物質を抽出する方法を開発。医薬品の原料として、すでに活用が始まっている。その際は、ユーカリの樹が茂るベトナムの森までカヌーで赴いたこともあるという。「研究を突き動かすのはいつだって好奇心です。それがある限り、どこへでも行きますよ。もっともベトナムの森では少々怖い思いもしましたが(笑)」

岩佐教授の好奇心は、まだまだとどまることを知らないようだ。

取材・文＝田井中麻都佳

取材後記

千葉大学で学位を取った後、天然物化学を究めたいと、世界中の研究所に手紙を書いたという若かりし日の岩佐教授。そのとき、なんのコネもないのに、最初に返事をくれたのが、オハイオ州立大学だった。そこで渡米しストリキニーネの合成などの研究成果を上げると、今度はシカゴ大学からオファーが来た。アメリカの懐の深さと、研究者ネットワークの強さを感じた瞬間だった。

その恩返しとして、現在、岩佐教授は留学生の受け入れを積極的に行う。研究室には、中国やモンゴル、ラオス、マレーシアなど、8カ国もの学生が在籍しているという。

「そうやって世界を知ることで、日本の良さを再認識できる。技術力の高さやモラリティの高さ、環境への配慮など、日本の良さをぜひ、世界に広めていきたい。そのために、現在、アジアでの日本語教育にも注力しているところです」と岩佐教授。

その好奇心は、研究だけでなく教育や環境にも広がっている。

Researcher Profile

Dr. Seiji Iwasa received Ph.D. degree in Engineering from Chiba University in 1991. After getting his Ph.D., he was engaged in research as Post Doctoral Research Associates in Ohio State University, University of Chicago, and ERATO respectively. Currently, Dr. Iwasa is a professor in Department of Environmental and Life Sciences at Toyohashi University of Technology. His research interests are asymmetric synthesis, carbene, diazo compound, natural product, and so on.

Reporter Profile

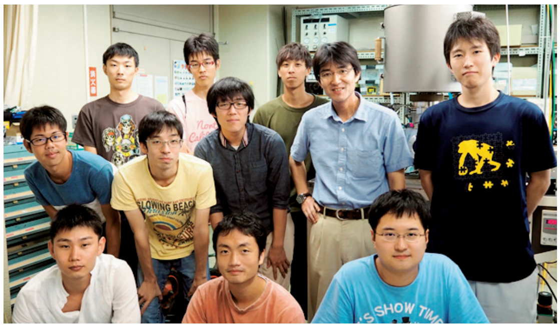
Madoka Tainaka is a freelance editor, writer and interpreter. She graduated in Law from Chuo University, Japan. She served as a chief editor of "Nature Interface" magazine, a committee for the promotion of Information and Science Technology at MEXT (Ministry of Education, Culture, Sports, Science and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

Unveiling the electron's motion in a carbon nanocoil

Development of a precise resistivity measurement system for quasi-one-dimensional nanomaterials using a focused ion beam

By Yoshiyuki Suda

Yoshiyuki Suda, in cooperation with researchers at the University of Yamanashi, the National Institute of Technology Gifu College, and Tokai Carbon Co., Ltd., has discovered how the electrical resistivity of carbon nanocoils (CNCs) depends on their geometry. The finding, which required development of a new resistivity measuring apparatus, paves the way for CNC-based nanodevices ranging from electromagnetic wave absorbers to nano-solenoids and extra-sensitive mechanical springs.

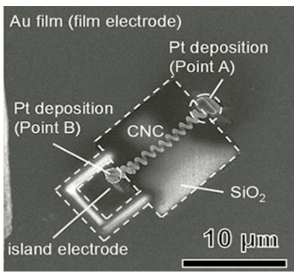


Yoshiyukii Suda (2nd from right, middle row) with his students

Carbon nanocoils (CNCs) are an exotic class of low-dimensional nanocarbons whose helical shape may make them suitable for applications such as microwave absorbers and various mechanical components such as springs. Typical thicknesses and coil diameters of CNCs fall within the ranges of 100–400 nm and 400–1000 nm, respectively, and their full lengths are much larger, on the order of several tens of micrometers. Despite earlier pioneering work, the relationships between the geometric shape of natural CNCs and their mechanical and electrical properties, particularly the electrical resistivity, are not well understood.

Now, Yoshiyuki Suda and his colleagues at Toyohashi University of Technology, University of Yamanashi, National Institute of Technology - Gifu College, and Tokai Carbon Co., Ltd. have established that the resistivity of CNCs increases with coil diameter. To make this discovery, it required the development of a precise resistivity measurement method, using a focused ion beam (FIB) and nanomanipulator technique to select a sample CNC with the desired coil geometry and then make firm electrical connections to the instrument's electrodes. All the resistivity data obtained with CNCs fits nicely with the curves predicted by a theory known as variable range-hopping (VRH), which is suitable for disordered materials at low temperatures.

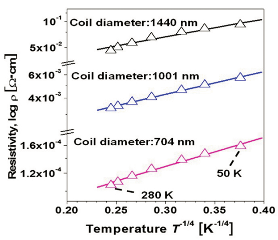
The research shows that the interior of the nanocoil contains material that affects its electrical properties. The scientists examined 15 individual CNCs, and three CNCs that had been artificially-graphitized to give them lower resistivity (G-CNCs). Although the resistivity of the CNCs increased with coil diameter, it was almost unchanged for the G-CNCs. As a consequence, for the CNCs with the largest diameters, the resistivity was almost two orders of magnitude larger than that of the graphitized versions.



Scanning electron microscope image of the resistivity-measuring electrical circuit, in which a single carbon nanocoil makes excellent contact with the electrodes.

This large discrepancy in the resistivity between CNCs and G-CNCs indicates a significant structural complexity inside the CNCs. The results imply that the interior of CNCs with large coil diameter is filled with a highly-disordered carbon network that consists of many small regions (known as sp2 domains) embedded in a sea of amorphous carbon. To verify this theory, the temperature dependence of the resistivity between 4 K and 280 K was examined. The resistivity data obeyed two different versions of the VRH theory; the regime in the temperature range of 50–280 K was found to be the so-called Mott-VRH version, while that in the range of 4–20 K was the Efros–Shklovskii-VRH version. Interestingly, the resistivity curves shifted smoothly between regimes as the coil diameter was changed.

"We first observed this behavior three years ago. Thanks to the efforts of two my students, we were able to include the resistivity data for G-CNCs and straight carbon nanofibers (CNFs), and compare them to the data for the CNCs", explains Associate Professor Yoshiyuki Suda, "I am very grateful to Prof. Hiroyuki Shima and Dr. Tamio Iida for joining this study. Together, we obtained the low-temperature measurement data and discussed it using the VRH theory. Eventually, we came to the conclusion that this behavior is a unique phenomenon for CNCs and can be fitted by VRH."



Dependence of the resistivity of carbon nanocoils on temperature, for different coil diameters. The graph's axes, log resistivity (ρ) and $T^{-1/4}$, are used to simplify the portrayal of the functional dependence. Solid lines in this figure show the best fit to the data with the Mott-VRH model.

The first author, Master's course student, Yasushi Nakamura, commented on how they went beyond the CNC resistivity measurements of other groups. "It was a long and challenging task. I had to prepare many single CNC samples using a focused ion-beam apparatus. Our finding was achieved by establishing a precise measurement system using a scanning electron microscope and acquiring resistivity data for many single CNCs."

The group's present results on resistivity are in qualitative agreement with their previous findings on the mechanical properties of CNCs: Tensile load experiments showed that their shear modulus increases with coil diameter. The positive correlation between the shear modulus and coil diameter is possibly caused by the fact that in large-diameter CNCs, the population of sp2 domains, which are fragile against shear stress, is reduced in comparison to small-diameter CNCs.

These results imply that, with nanocoils, the resistance as well as the inductance are defined by geometric factors. In particular, coil diameter, pitch, and length are important. The correlation found can be used to improve control over the peak frequency of electromagnetic wave absorption, in which a particular range of frequencies (~GHz) is absorbed, dependent on the impedance properties.

These findings pave the way for CNC-based nanodevices, ranging from electromagnetic wave absorbers to nano-solenoids and extra-sensitive mechanical springs.

This work was partly supported by

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- The Toyota Physical and Chemical Research Institute.

Reference

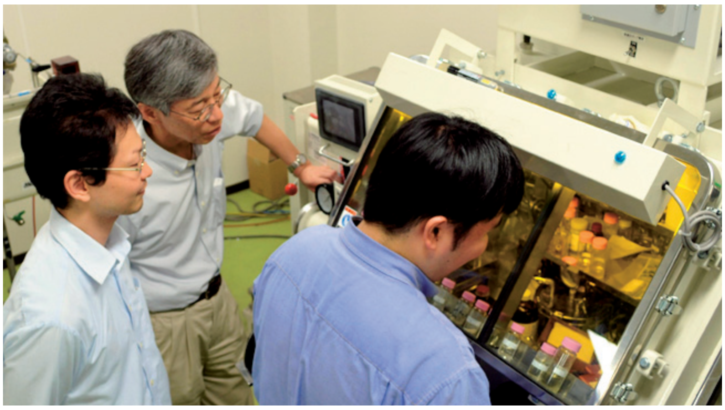
Yasushi Nakamura, Yoshiyuki Suda, Ryuji Kunimoto, Tamio Iida, Hirofumi Takikawa, Hitoshi Ue, and Hiroyuki Shima (2016). Precise measurement of single carbon nanocoils using focused ion beam technique, Applied Physics Letters, 108, 153108. 10.1063/1.4945724

Towards building next-generation batteries using a pigment electrode

Electrode design of next-generation batteries using Prussian blue and its analogues

By Tomohiro Tojo

Tomohiro Tojo and his colleagues have demonstrated the properties of calcium ion batteries (CIBs) created using pigment electrodes such as Prussian blue and its analogues. The CIBs showed excellent cyclability of discharge and charge in a calcium-based organic electrolyte. This is thought to derive from strong atomic bonds in Prussian blue structures, which possess movable pathways for large-sized ions in three dimensions. Such unique structures have excellent potential for application in a new generation of batteries.



Tomohiro Tojo (left of picture) with his colleagues

Calcium ion batteries (CIBs) have attracted much attention as the next-generation batteries likely to replace lithium ion batteries (LIBs). This is because the theoretical capacity of CIBs is twice that of LIBs. This doubled capacity can be explained by the difference between monovalent and divalent ions. In addition, CIBs possess advantages such as lower cost and higher safety because calcium is more abundant than lithium and because CIBs have a higher melting point than LIBs. However, there is one major obstacle to the application of CIBs. It is hard to find a suitable electrode material in which calcium ions can be inserted and extracted reversibly because of the relatively large ionic radius of calcium ions (112 pm) as compared to that of lithium ions (76 pm).

In this study, Tomohiro Tojo and his colleagues at the Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, employed Prussian blue (PB) and Prussian blue analogues (PBAs) as CIB electrodes because they possess large sites for inserting and extracting large-sized ions, as shown in Fig. 1. Up to now, using PBAs as an electrode material, the electrochemical behaviors of sodium ions corresponding to the radius of calcium ions have been examined in organic and inorganic electrolytes. These reports have shown reversible insertion and extraction of sodium ions into and from PBA structures.

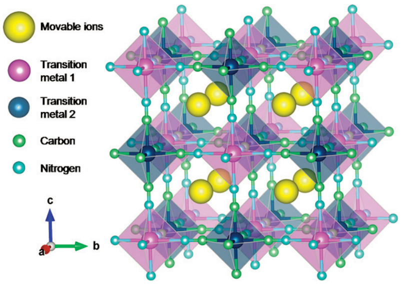


Figure 1. Crystal structure of Prussian blue and its analogues

The research team investigated the electrochemical performance of several PBA electrodes in order to determine whether calcium ions in an organic electrolyte exhibit either reversible or irreversible insertion and extraction into and from the crystal structure. Reversible capacities of 40–50 mAh/g were observed at a low current density, as shown in Fig. 2(a). In Fig. 2(b), the Coulombic efficiencies, which are defined as the ratio of the amount of insertion (discharge) and extraction (charge) of calcium ions, were observed to have a constant value of 90% after the 3rd cycle.

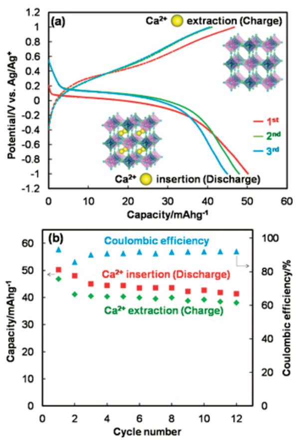


Figure 2.
(a) Discharge-charge profiles of a Prussian blue analogue electrode in a calcium-based organic electrolyte and (b) cycled capacities with discharge-charge capacity ratio

The results shown in Fig. 2 demonstrate the excellent cyclability of the PBA electrodes, even though the reversible capacities were half the theoretical capacity. The researchers investigated the reason for the high reversibility using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The reversibility is explained by the durable structure of the PBAs and their excellent charge balance during the insertion and extraction of calcium ions.

This data suggests that Prussian blue (PB) and Prussian blue analogues (PBAs) may be proposed as feasible electrode materials for CIBs, although additional investigation is needed in order to enhance the reversible capacities still further. The researchers plan to carry out further study to improve the performance of CIBs relative to LIBs.

This work was partially supported by

- Grant-in-Aid for Challenging Exploratory Research (No. 15K13947) by MEXT.
- Grant-in-Aid for Scientific Research (B), No. 24360109 by MEXT

Reference

Tomohiro Tojo, Yosuke Sugiura, Ryoji Inada, and Yoji Sakurai (2016). Reversible Calcium Ion Batteries Using a Dehydrated Prussian Blue Analogue Cathode, Electrochimica Acta, 207, 22-27, 10.1016/j.electacta.2016.04.159

Can robots recognize faces even under backlighting?

An adaptive contrast adjustment for illumination-invariant face appearance

By Jun Miura

Jun Miura and his colleagues have developed a novel technique to address the problem of vision-based face detection and recognition under normal and severe illumination conditions. This technique contributes to help robotic systems that use face information for providing user-dependent services to work well under a large variety of illumination conditions.

Jun Miura (right of picture) with PhD candidate Bima Sena Bayu Dewantara

Vision-based face detection and recognition is one of the most rapidly growing research areas in computer vision and robotics and is widely used in several human related applications. However, vision-based face detection and recognition has been shown to be effective only under normal illumination conditions. In developing an algorithm for face detection and recognition, it is crucial to consider both normal and severe illumination conditions. One approach is to convert face images under various illumination conditions into ones with invariant face appearance while preserving the face-specific characteristics such as texture and facial features.

Now, researchers at the Department of Computer Science and Engineering at Toyohashi University of Technology have developed a novel technique to adaptively adjust the effect of lighting on human faces by employing an extended reflectance model. The model has one variable (illumination ratio), which is controlled by Fuzzy Inference System (FIS). To cope with a vast variety of illumination conditions, the FIS rule was optimized using Genetic Algorithm (GA).

The first author PhD candidate, Bima Sena Bayu Dewantara, explained, “To eliminate the effects of light, image contrast should be adjusted adaptively. To produce an invariant face appearance under backlighting, for example, cheeks need to be brightened, while the eyeballs must be kept dark. Such an adaptive contrast adjustment can be performed using the developed reflectance model, and we have shown that a combination of Fuzzy Inference System (FIS) and Genetic Algorithm (GA) is very effective for implementing the model.”

Professor Jun Miura said, “By just adding this contrast adjustment to present face recognition systems, we can significantly improve the accuracy and performance of face detection and recognition. Moreover, this adjustment runs in real-time, and therefore, it is appropriate for real-time applications such as robot and human-interaction systems.”

A face not only provides a person’s identity but also provides other information such as a person’s focus of attention and the degree of tiredness. Obtaining such information is useful for smooth human–machine interaction, and researchers expect that the proposed contrast adjustment method will also be useful in various situations, especially under severe illumination conditions.

This study was partly supported by a Grant-in-Aid for Scientific Research No. 25280093 by JSPS, Japan.

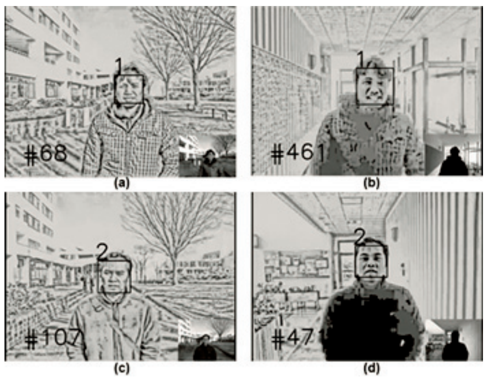
Reference

Bima Sena Bayu Dewantara and Jun Miura (2016). OptiFuzz: A robust illumination invariant face recognition and its implementation, Machine Vision and Applications, DOI: 10.1007/s00138-016-0790-6.

Input Images

Processed Images

Result of the illumination invariant face processing using Yale B Extended database: input images (top) and processed images (bottom).



R Results of illumination invariant face recognition for real implementations: (a) person #1 outdoor, (b) person #1 indoor, (c) person #2 outdoor and (d) person #2 indoor. Small image in the bottom-right side of each image is the input image.

Sociable Dining Table

Learning from the Wizard to enable a Human-Robot social interaction adaptive to individual preference

By Khaoula Youssef

To effectively design robots that leverage available non-expert human scaffolding, we need to understand how humans naturally teach. Ph.D. candidate Khaoula Youssef and her research group in Toyohashi University of Technology demonstrated how we can ecologically extract interaction patterns and integrate an adaptive architecture into robots enabling them to adapt to emerging online human knowledge. The approach consists of two experiments: a human-human experiment (Wizard-of-Oz) to explore how people build a protocol of communication, and a human-robot interaction (HRI) experiment to validate how an actor-critical architecture suggested in the first experiment enabled the adaptation to individual preference.

When robots are supposed to learn a task, much engineering by technical experts goes into determining how the industrial robots should be adjusted to the specific task. However, social robots include those that interact with non programmers. Because human beings are a largely untapped source of knowledge and guidance during the learning process, designing a task-specific designed robot is difficult.

Thus, to effectively design such social robots with relatively natural interfaces that allow anyone including non-programmers (non-experts) to guide the learning process of a robot, understanding how humans naturally teach is important.

Ph.D. candidate of Khaoula Youssef and her research group from the Interaction and Communication Design (ICD) Lab at Toyohashi University of Technology could identify the commonly mirrored patterns and strategies used by humans in a human-human interaction context by conducting a Wizard-of-Oz (WOz) experiment.

In the experiment, the first human in room (A) knocks on the table to make a robot called Sociable Dining Table (SDT) exhibit certain behavior. These knocking sounds are translated by the second human, the robot's remote controller located in room (B). The controller does not recognize these as human knocking patterns, while the human ignores the fact that the controller controls the robot using his/her knocking. It was found from the experiment that incrementally people modulated their knocking, which suggests that they understood over time that they needed to use simple commands to make the robot behave according to their intentions (systematized input means systematized output).

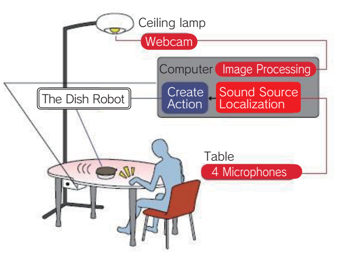
Youssef Khaoula said "We could identify specific patterns of interaction based on the WOz experiment. For example, sometimes the controller auto-criticized his choice and changed the robot's behavior without being stimulated by any knocking (confusion state). The knocker could learn to read this situation and adapt their behavior to implicitly help the controller by composing the previously sent command (remedial knocking pattern). Thus, we decided to use the actor-critic architecture which is a reinforcement-based algorithm."

After implementing the actor-critic architecture, a Human-Robot Interaction (HRI) experiment was conducted to verify whether the human (knocker) could interact with the robot to translate the emerging knocking patterns in the same way as the previous experiment. Here, the robot is autonomous and does not require a controller. The results indicated that the autonomous robot using the actor-critic algorithm could indeed establish a communication protocol when interacting with a non-programmer.

The robot is not designed to be task-specific, but it adapts to the user's method which may empower the robot and makes the interaction natural. The methodology serves as an inspirational technique that roboticists building robots for non-programmers could follow to build useful and easy to use minimally designed robots imbued with the capability to interact naturally with the human.

This research is supported by Grant-in-Aid for scientific research of KIBAN-B (26280102) from the Japan Society for the Promotion of Science (JSPS).

Khaoula Youssef (2nd from right, upper row), supervisor Prof. Michio Okada (3rd from left, lower row) and ICD lab members including international students from four different countries



The overall architecture of the SDT: the human's knock is detected by four microphones while the robot executes different behaviors using the servomotor

Reference

Youssef Khaoula, Asano Takahiro, De Silva P. Ravindra S. and Okada Michio (2016). Sociable Dining Table: Meaning Acquisition Exploration in Knock-Based Proto-Communication, International journal of social robotics, 8(1), 67--84. 10.1007/s12369-015-0314-y.

カーボンナノコイルの電子輸送機構の解明

集束イオンビーム装置を利用した準一次元ナノ材料のための精密な抵抗率測定系の開発

須田　善行

電気・電子情報工学系　須田善行准教授は、山梨大学、岐阜高専、東海カーボンの研究者と共同で、初めてカーボンナノコイル（CNC）の電気抵抗率とコイル形状との関係を明らかにしました。この研究成果は新たな抵抗率測定系を開発することによって初めて成し遂げられました。研究での発見はCNCを用いたナノデバイス—電磁波吸収体、ナノソレノイド、超高感度コイルばね—への道を開くものとなります。

カーボンナノコイル（CNC）はらせん構造をもつ低次元カーボンナノ材料です。典型的なCNCは、ファイバー直径が100から400ナノメートル、コイル直径が400から1000ナノメートルであり、全長は数十マイクロメートルあります。CNCのらせん構造は様々な応用—電磁波吸収体やエネルギーデバイスの材料—が期待されています。こうした応用のために、CNCの機械的・電気的特性を明らかにすることは重要です。いくつかの先駆的な研究例はあるものの、CNCの形状とその電気抵抗率との関係は未解明のままでした。

豊橋技術科学大学、山梨大学、岐阜高専、東海カーボンの研究者らはCNCの電気抵抗率がコイル直径によって増大することを見出しました。それにあたり、集束イオンビーム装置を使用してCNC抵抗率の精密な測定系を開発しました。その測定系は、所望のコイル形状をもつCNCを測定用試料として選択し、測定用電極とそのCNCとを強固に接触させることができるものです。測定されたCNCの電気抵抗率データはバリアブルレンジホッピング（VRH）理論に基づく曲線とよい一致を示しました。

開発した装置により、15本の単一CNCと3本の黒鉛化処理CNC（G-CNC）とを測定し、CNCの電気抵抗率がそのコイル径によって増加することを見出しました。一方、G-CNCの電気抵抗率はコイル径によらずほぼ一定でした。最大のコイル径をもつCNCの電気抵抗率はG-CNCの電気抵抗率よりおよそ2桁高い値を示しました。CNCとG-CNCとの間の電気抵抗率の大きな差はCNC内部の構造に起因するものと考察されました。

本研究の一部は、科研費24360108，25390147，15K13946と、豊田理化学研究所の支援を受けて実施されました。

顔料電極を用いた次世代電池の構築に向けて

プルシアンブルー系電極を用いた次世代電池の設計

東城　友都

電気・電子情報系　東城友都助教らの研究グループは、顔料であるプルシアンブルー(PB)・プルシアンブルー類似体(PBA)を電極材料に用いて、カルシウムイオン電池(CIB)の充放電試験を行いました。その結果、カルシウム系有機電解液中では、CIBの充放電サイクル性能が優れていることを示しました。これは、PBの原子同士が強固に結合しており、PBが大径のイオンを3次元的に伝導させるための経路を持つためであることが示唆されました。このような特異構造をもつ電極材料が次世代電池の開発に重要となります。

カルシウムイオン電池(CIB)は、理論上、リチウムイオン電池(LIB)の二倍の容量を示すため、LIBを超える次世代電池として注目を集めています。この容量の違いは、可動イオンに1価、2価のイオンを用いている違いによるものです。またCIBは、カルシウムの埋蔵量がリチウムに比べて多いことや融点が高いことから、LIBよりも低価格、高安全性な電池であることが考えられます。しかしながら、CIBの実現にはまだ問題点があります。それは、カルシウムイオン(112　pm)がリチウムイオン(76　pm)よりもイオン径が大きいために、カルシウムイオンを可逆的に挿入・脱離できる電極材料が少ないことが挙げられます。

そこで東城友都助教らの研究グループは、図1に示すように、大径のイオンを挿入・脱離することが可能とされるプルシアンブルー(PB)およびプルシアンブルー類似体(PBA)をCIB電極に採用しました。現在までにカルシウムイオンと同程度のイオン径であるナトリウムイオンを用いて、PBA電極の電気化学特性が有機電解液中・無機電解液中で評価されており、ナトリウムイオンの可逆的な挿入・脱離が確認されています。

また、ナトリウムイオンの代わりにカルシウムイオンを用いて、カルシウムイオンがPBAに可逆的に挿入・脱離するかどうかを調査するため、PBA電極の性能評価を行ないました。図2 (a)に示す通り、その充放電特性から40-50mAh/gの可逆容量を確認しました。また図2　(b)に示す通り、3サイクル以降のクーロン効率*は約90%で一定となりました。

図2の結果から、可逆容量は理論容量の半分程度ではあるが、クーロン効率すなわち、サイクル性能は優れていることが確認されました。このサイクル性能は何に起因しているのかX線回折(XRD)およびX線光電子分光法(XPS)により調査を行なった結果、PBAの壊れにくい構造と良好な電荷バランスに由来していることが判明しました。

本研究ではCIBに最適な電極材料として、プルシアンブルー(PB)およびプルシアンブルー類似体(PBA)を提案しましたが、PBA電極の可逆容量の向上については、更なる研究が必要です。今後は、LIBを超えるCIBの材料研究を引き続き進めていく予定です

*クーロン効率：　クーロン効率は、充電容量(カルシウムイオン脱離量)/放電容量(カルシウムイオン挿入量)から求められる百分率で、この数値が100%に近い程、電池容量の損失が少ないことを示す。

本研究は文部科学省・科研費・挑戦的萌芽研究No. 15K13947の一部および、文部科学省・科研費・基盤研究(B)　No.　24360109の支援を受けて遂行されました。

ロボットは逆光でも人の顔を見分けられるか？

顔の見え方を照明条件によらず一定にするための適応的なコントラストの調整

三浦　純

情報・知能工学系　三浦純教授らの研究グループがさまざまな照明条件下で顔の発見と認識が可能になる新たな手法を開発しました。この手法により、顔の特徴を使って利用者を認識し、利用者に応じたサービスを提供するロボットが、厳しい照明条件下でも動作できるようになります。

画像による顔の発見と認識は、顔認証によるセキュリティシステムや人をサポートするロボットなどの応用に幅広く利用されています。これまでの多くの手法は通常の照明下でのみ有効でしたが、実際の応用を考えると通常の照明下だけでなく厳しい照明の下でも動作することがとても重要です。そのための一つのアプローチは、さまざまな照明下での顔の画像を、顔特有の模様や特徴を維持しつつ一定の見え方になるように変換することです。例えば、逆光下では顔全体が暗くなりますが、画像変換により、頬は明るくする必要がありますが、瞳は暗いままにしておかなければなりません。

そこで、本学の情報・知能工学系の研究グループ（博士後期課程学生　Bima　Sena　Bayu　Dewanntaraおよび三浦教授）は、拡張された光の反射モデルを用いて照明の影響を適応的に調整する新たな手法を開発しました。このモデルは調整可能な一つの変数（illumination　ratioと呼ぶ）を持ち、その変数をファジィ推論システムによって制御します。そして、さまざまな照明条件に対応するため、推論システムが利用するファジィ推論規則を遺伝的アルゴリズム（GA）によって最適化しておきます。

提案する画像変換処理を現存の顔認識システムに追加するだけで、顔の発見と認識の性能を大幅に向上させることができます。さらに、この変換は実時間で行えるので、ロボットや人とやり取りをするシステムのような実時間動作が必要な応用に適しています。

顔は人の識別に役立つだけでなく、注意を向けている方向や疲れの程度など人のさまざまな情報を提供します。そのような情報を得ることは、人間と機械の間の快適なやり取りに有効であり、今回開発した顔画像変換手法はさまざまな応用において、特に厳しい照明条件下で有効に利用されることを期待しています。

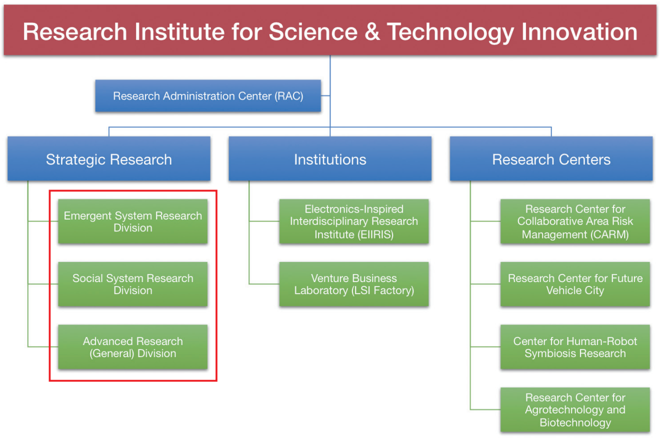
本研究成果は、平成28年7月15日（金）にMachine Vision and Applications誌上に掲載されました。

本研究の一部は科研費25280093の支援を受けて実施されました。

Pick Up

TUT launch Research Institute for Science & Technology Innovation along with 16 innovative research projects

In April 2016 TUT unveiled a new strategic research institution along with, 16 cutting-edge and innovative research projects it will oversee. All of these projects are intended to be of social use, and are collaborative efforts with leading industry, companies and institutions. The projects were chosen carefully from 25 applications proposed by the board members of the institute, based on an analysis of various factors, such as an evaluation of matching funds with the collaboration partner, the mission and role, and the expected impact of the project.



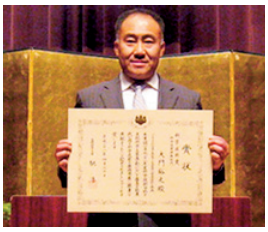
	Emergent System Research Division	Project Leader in TUT
1	Research Project for Social Implementation of Relation-oriented Robots	Michio Okada
2	TUT-ASMO Advanced Motion Technology Laboratory Project	Jun Miura
3	Development of Next Generation Contaminant Detection Technology	Saburo Tanaka
4	High-Frequency Semiconductor Circuit Serendipity for Wireless Power Transfer	Takashi Ohira
5	Development of novel bio-sensors using Sensor / MEMS technology	Kazuhiro Takahashi
6	Advanced tool Coating Technological laboratory, OSG-TUT collaboration (ACTO)	Hirofumi Takikawa
7	Road Marking 2.0 Project	Kojiro Matsuo
	Social System Research Division	
1	Research on Societal Implementation of Supporting Multilingual Information Outbound	Hitoshi Isahara
2	Development of an outdoor cleaning robot usable in a recycle center	Naoki Uchiyama
3	Development and implementation of a disaster detection and disaster prevention information sharing system in order to support the Tokai region in the case of a massive earthquake	Taiki Saito
4	Research for Production and Utilization of Biomass	Hiroyuki Daimon
5	New agriculture promotion plans for agriculture development in East Mikawa region	Takanobu Inoue
6	Investigation of mechanism of water pollution material runoff	Kuriko Yokota
	Advanced Research (General) Division	
1	Innovative Advanced Sensor Processing and Ion-Biology	Kazuaki Sawada
2	Research on Experimental Cognitive Science of Psychological Brain Mechanisms	Shigeki Nakauchi
3	Multiferroic Materials Laboratory for Advanced Applications	Atsunori Matsuda

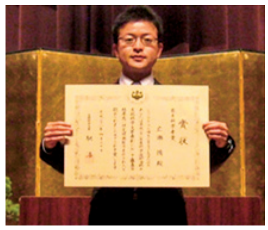
Commendations for Science and Technology awarded by the Minister of Education, Culture, Sports, Science and Technology

This award is given to researchers who achieve significant results in the study of science and technology. On April 20th 2016 two researchers from TUT received this award.

Science and Technology Promotion Category
Professor, Hiroyuki Daimon
"Promotion of a recycling composition technology by production and utilization of Biomass"

The Young Scientists' Prize
Assistant Professor,Yuu Hirose
"Analysis of Complementary Chromatic Acclimation Process of Cyanobacteria"


Professor Daimon


Assistant Professor Hirose

Prestige lecture held in TUT by 2010 Nobel laureate Professor Akira Suzuki

Akira Suzuki, Nobel laureate in Chemistry 2010, was invited to TUT on 30th Jun 2016 to give a Prestige Lecture entitled "Cross-coupling Reactions of Organoboranes: An Easy Way for C-C Bonding". This lecture was facilitated by the TUT leading graduate school program students and an interactive session with the program students was held after the lecture.

Before presenting the lecture, he had a chance to meet high school students invited to TUT from Asian countries. The students, from 9 top high schools across 5 different countries, were very excited by this rare opportunity and were greatly encouraged to come to Japan to study engineering, technology and science.

International Conferences organized by TUT

As a Top Global University of Japan, Toyohashi University of Technology organized or chaired the following International Conferences:

APCOT 2016
Asia-Pacific Conference of Transducers and Micro-Nano Technology 2016
June 26-29, 2016, Kanazawa Japan
General Chairman: Professor Kazuaki Sawada, Toyohashi University of Technology

WFC 2016
The 72nd World Foundry Congress
May 21-25, 2-16, Nagoya Japan
Co-Chairman: Professor Kazuhiro Terashima, Toyohashi University of Technology

ICAICTA 2016 / 4th IGNITE
The 2016 International Conference on Advanced Informatics: Concepts, Theory and Application
August 16-19, 2016, Penang Malaysia
Organized by: Toyohashi University of Technology (Japan), Universiti Sains Malaysia (Malaysia), Institut Teknologi Bandong (Indonesia) and Brapha University (Thailand)

WFC 2016 in Port Messe Nagoya

TUT Research
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