

NAMIS international Autumn school 2016

12 -16 September

"Micro/nano technologies for future health, environment and sustainability"



Institute of Industrial Science The University of Tokyo



Principal of NAMIS international Autumn school 2016



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For participants of NAMIS international Autumn school 2016

Welcome to Institute of Industrial Science of the University of Tokyo. I am glad to have many Ph.D students and young researchers from NAMIS partners participating NAMIS Autumn School 2016 from all over the world.

We have planned:

- Lectures for learning the state-of-the-art of MEMS research and applications and for expanding your view on related areas,
- Experiments for experiencing the reality of what is written,
- Poster presentation for sharing your results with others and earning presentation techniques,
- · Lab tours for introducing our research environment,
- Field Trips for getting to know various aspects of Japanese culture with a view to possible future scholastic long term stays in the country,
- Social events for getting acquainted with students and professors from all over the world,
- Free time for active interaction between the multinational participants, and getting to know Japan.

It is imperative that participants attend all the programs in an active manner, interact with as many people as possible, get well prepared for presentations and challenge many things.

I would like to appreciate the financial support from IIS and Core to Core programs of JSPS. I also thank Profs. Kawakatsu, Nomura, Matsunaga and Okitsu, and Dr. Kobayashi, and secretaries for their dedicated efforts



preparing the School.

Please, enjoy the School.

Beomjoon KIM, Dr. Eng. Professor

CIRMM (Centre for Interdisciplinary Research on Micro-Nano Methods)

Institute of Industrial Science, The University of Tokyo.

Dos and Don'ts during School

Dos

- Asking questions
- Talking to people from other counties during break, lunch, dinner, party, and excursion
- Looking for new ideas and techniques that will benefit your future work
- Taking leadership in group activities such as experiment, discussion and final presentation
- Working hard on your posters and one-minute flash presentation
- Post studies by visiting homepages of lectures and bibliographical work.

Don'ts

- Escaping from lectures and other events (host labs will be notified of this conduct)
- Communicating via PCs and cellular phones during lectures (No e-mail, twit, facebook, etc.)
- Web-surfing during lectures
- Sticking on colleges from your own country
- Sitting alone silently

Things to prepare for the last day

At the last day of the school, we will ask each group to make a 20 min presentation with Microsoft Powerpoint slides.

The presentation should include the answers to the following questions:

- (0) Group number
- (1) How were your results of both Dr. Shirakawa's experiment and NAMIS challenge? What did you learn?
- (2) What is the most impressive event during this school including the free time?
- (3) Over all, how do you feel about this NAMIS School? Please let us know your candid impressions and comments
- (4) Any suggestions on how the school might be organized next year? Any field of interest one might add?

It would be nice if you could make the slides with photos/movies; we recommend you to take photos (and movies) occasionally.



Access information Institute of Industrial Science (IIS)

The school is held at the Institute of Industrial Science, the University of Tokyo, Komaba II research campus. You will find all the information to reach the research campus here: http://www.iis.u-tokyo.ac.jp/access e/access e.html





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Access information

Airports to National Olympics Memorial Youth Center

Traffic guide from airports to National Olympics Memorial Youth Center is available on the following URL: http://nyc.niye.go.jp/en/access-train/



Adress: 3-1. Yoyogi Kamizono-cho, Shibuya-ku, Tokyo 151-0052 Phone: +81-3-3469-2525

Access information National Olympics Memorial Youth Center to IIS





Your lodging building is on the north side of Youth Education National Olympics Memorial Youth Center (surrounded by blue broken line).

First, you go through the main gate, turn right and cross the pedestrian bridge. Go 100 meters, turn left and cross the railroad. After walking 80 meters, turn right and go 90 meters, you can find Sangubashi Station.

After buying your ticket and entering the ticket gate, cross the left side bridge across railway, and go to the opposite side of the platform. Then you can get on the train towards the Institute of Industrial Science, IIS.

Now you get off at the 3rd stop, Higashi-Kitazawa Station. After exiting the ticket gate, turn right, and go 400 meters along the street. You can find the gate of IIS at

your right side.

Building "An" is the 4th building from the gate.

Here are some Japanese characters meaning the names of the center and the stations:

国立オリンピック記念青少年総合センター;

Youth Education National Olympics Memorial Youth Center

参宫橋; Sangubashi Station

東北沢; Higashi-Kitazawa Station







Sep 14 Wed Dw 601	Sep 15 Thu Dw 601	Sep 16 Fri Eneos Hall	
Prof. Kawakatsu	Prof. Kim	Prof. Nomura	8.30
			0.50
			9:00
L(I) Prof. Bosseboeut		Lecture 13	9:15
Lecture 07	Lecture 10	Prof. Takamiya	
Prof. Peter	Prof. SJ Kim		9:45
		Lecture 14	10:00
Lecture 08	Lecture 11	Prof. Mizoguchi	
Prof. Ammar	Prof. BJ Kim		10:30
Coffee break	Coffee break	Coffee break	10:45
			-11:00
Lecture 09 Prof. Kowakateu	Lecture 12 Prof. Forrigno	Lecture 15	
PIOI. Nawakatsu	FIOI. Ferrigilo	Prof. Joly	11.45
			12:00
Lunch	Lunch	Lunch	
@ E-lounge	@ E-lounge	@ E-lounge	
			13:00
		Lecture 16	
		Prof. Mita	13:30
	Lab Tour		13:45
	(Takeuchi, Fujii,	Lecture 17	
	Matsunaga Labs)	Prof. Timofeev	
			14:30
		Coffee break	
			15:00
KAMAKURA visit	NAMIS challenge		
guided by			
Prof. Kim and			16.00
Drof Kowakatau		Group presentation	10.00
Prof. Rawakatsu			
	Preparation for		
	Group presentation		17:00
	Group presentation		
		Awards and Closing	
			17:45
]		18:30
		Farewell Party	
			20:30

Lab Tour

Schedule

Monday, 12th Sep., 2016

Group	13:30 - 13:50	13:50- 14:10	14:10 - 14:30
1	Fujita Lab	Fujita-Toshiyoshi Lab	Kim Lab
2	Fujita Lab	Fujita-Toshiyoshi Lab	Kim Lab
3	Kim Lab	Fujita Lab	Fujita-Toshiyoshi Lab
4	Kim Lab	Fujita Lab	Fujita-Toshiyoshi Lab
5	Fujita-Toshiyoshi Lab	Kim Lab	Fujita Lab
6	Fujita-Toshiyoshi Lab	Kim Lab	Fujita Lab

Thursday, 15th Sep., 2016

Group	13:30 - 13:50	13:50- 14:10	14:10 - 14:30
1	Takeuchi Lab	Fujii Lab	Matsunaga Lab
2	Takeuchi Lab	Fujii Lab	Matsunaga Lab
3	Matsunaga Lab	Takeuchi Lab	Fujii Lab
4	Matsunaga Lab	Takeuchi Lab	Fujii Lab
5	Fujii Lab	Matsunaga Lab	Takeuchi Lab
6	Fujii Lab	Matsunaga Lab	Takeuchi Lab

Location

	To start lab tour	For lab tour
Fujita Lab	FwB05	FwB05
Fujita-Toshiyoshi Lab	Ee308	Ee308
Kim Lab	Dw304	DeB02
Takeuchi Lab	Komaba Open Laboratory (KOL) 1st Floor	KOL M202
Fujii Lab	Fw603	Fw603
Matsunaga Lab	An601	An601



Lecture List

No					
NU.	Leclurei				
01	Hiroyuki Fujita	Overview of MEMS/NEMS Research			
02	Hanns Zappe	Optical micro/nano systems for health and environmental sensing			
03	Noo Li Jeon	Microfluidic Orgain-on-a-Chip Platform			
04	Tetsuya Kobayashi	Mathematics & Informatics for Quantitative Biology			
05	Alain Bosseboeuf	Processes and characterization tools for low temperature wafer-level vacuum packaging			
06	Masumi Yamada	Microfluidics for hepatic tissue engineering:New 3D cell- culture approaches using microfibers and microparticles produced by microfluidic technologies			
07	Yves Alain Peter	Optical Microresonators			
08	Mehdi Ammar	Integrated bio-functionalization techniques in fluidic MEMS: How to play with magnetic nanoparticles for immuno-assays			
09	Hideki Kawakatsu	Towards Atomic Force Microscopy with Real Time Mapping of Morse Parameters			
10	Sung Jae Kim	Nonlinear Nanoelectrokinetic Ion Concentration Polarization and its Energy/Environmental/Bio Applications			
11	Beomjoon Kim	Dissoluble Microneedle patch for transdermal drug delivery systems			
12	Rosaria Ferrigno	Dielectrophoresis and magnetophoresis integration and applications in microfluidic devices			
13	Makoto Takamiya	Circuit and System Design for Organic Electronics			
14	Teruyasu Mizoguchi	TEM: Atomic Resolution Microscopy and Spectroscopy			
15	Laurent Joly	Micro/nanofluidics-based sustainable energy harvesting using electrokinetic effects: recent advances and remaining challenges			
16	Yoshio Mita	"MEMS-de-Piano": a short turn-around-time experimental course in UTokyo Nanotechnology Platform			
17	Andrey Timofeev	Technology of far-infrared detectors and sub-THz cameras at VTT Technical Research Centre of Finland			
L(I)	Alain Bosseboeuf	The NAMIS international network: a short overview			

Overview of MEMS/NEMS Research

Hiroyuki Fujita, Ph.D.

CIRMM, Institute of Industrial Science, The University of Tokyo, Tokyo, Japan E-mail: fujita@iis.u-tokyo.ac.jp

This lecture intends to share the common base for categorizing various knowledge on MEMS and NEMS among those who attend the NAMIS School; this school is organized by Nano and Microsystem research network in order to give students and young researchers for learning latest research achievements as well as for getting acquainted with colleges having different culture and backgrounds. You will take the best advantage of the school by actively participating lectures, experiments, lab visits and events.

I will start my lecture with brief history of MEMS research. Then I will provide you a frame of reference with which you can classify the knowledge on MEMS and NEMS. For example, when you read a paper, its content may cover many aspects of MEMS, e.g. materials, device design, and its performance for a specific application. You need to extract knowledge in each category, the part of which is shown in the Table, and relate it to other works in the same category; this procedure will clarify you memory and help you remember what is known in the field.

Category	Sub-category
MEMS technology	Bulk micromachining, surface micromachining, CMOS-MEMS, bonding
Material	Metal, semiconductor, insulator, polymer, bio
Device	Physical sensor, bio/chemical sensor, actuator, 3-D microstructure
Design[1]	Structural shape & dimension, process sequence, material choice, modeling & analysis
Application	Sensing, optics, microfluidics, RF, energy harvesting
NEMS	Self-assembly (regular, selective), quantum effect, near-field effect, meta material,
	molecular/atomic interaction & dynamics
Hetero integration	over scale, material and process

References

[1] S. D. Senturia, "Microsystem Design" Springer (2001)



Biography

Hiroyuki Fujita is Professor (1993-present) and served as the Deputy Director (2009-2012) of the Institute of Industrial Science (IIS), The University of Tokyo. He also served the Director of the Center for International Research on Micronano Mechatronics (2000-2016). He received the B.S., M.S. and Ph.D. degrees from Department of Electrical Engineering of The University of Tokyo, Tokyo, Japan in 1975, 1977 and 1980, respectively. He joined IIS as an assistant professor just after earning his Ph.D. degree. He stayed in MIT as a Research Scientist (1983-1985) and in UC Berkeley as a Russell Severance Springer Professor in 2015. He received M. Hetenyi Award of Experimental Mechanics from the Society for Experimental Mechanics in 1986, Chevalier de l'Ordre des Palmes

Academiques from Government of France in 2001, The Prize for Science and Technology in Research Category from Japanese Ministry of Education, Culture, Sports, Science and Technology in 2005, Outstanding Achievement Award from The Institute of Electrical Engineers of Japan in 2005, and The Yamazaki-Teiichi Prize from Foundation for Promotion of Material Science and Technology of Japan in 2013. He is currently engaged in the investigation of MEMS/NEMS and applications to bio and nano technology as well as energy harvesters.

Optical micro/nano systems for health and environmental sensing

Prof. Hans Zappe Gisela and Erwin Sick Chair of Micro-optics Department of Microsystems Engineering University of Freiburg, Germany

COURSE SUMMARY

Micro and nanosystems are playing an increasingly important role in medical diagnostics, health monitoring and environmental sensing. Among these, optical systems are of particular interest due to the varied properties of light which can be used for sensing, in addition to the fundamentally non-contact nature of optical interactions. The field of optics in medicine and sensing is thus a very wide one, and we will consider only a few aspects of it here.

This short course will address the use of three novel micro-optical system concepts for medically-relevant diagnostics and environmental monitoring, all employing new materials and advanced microfabrication techniques.

- **Implantable blood-pressure monitors** The availability of highly-miniaturized optoelectronic light sources and detectors, coupled with microfabrication and packaging on flexible, biocompatible polymer substrates, has allowed the realization of compact, implantable optical sensors which measure displacement of blood vessels as well as varying composition of blood itself. These photoplethysmographic sensors enable continuous, high-precision monitoring of blood oxygenation, hemoglobin concentration as well as blood pressure.
- **Tunable optics for endoscopy** The silicon optical bench, an assembly technique which allows assembly of complex optical systems in an ultra-miniaturized form, has enabled high-performance optically-tunable, multi-modal optical imaging systems to be entirely incorporated into endoscopes. As a result, a combination of wide-field imaging, optical coherence tomography, confocal microscopy and fluorescence microscopy can be integrated into a single endoscopic measurement head for intracorporeal diagnostics.
- Large-area polymer sensor networks New developments in polymer materials coupled with advanced high-resolution printing technologies now allow large-area printing of complete integrated optical circuits on a flexible, all-organic foil. These waveguide-based circuits may be configured as high-resolution interferometric sensors, enabling two-dimensionally distributed sensing of a wide variety of environmentally-relevant compounds.

For each of these systems, we will discuss the functionality and structure, also describing the microsystems materials and fabrication techniques which play a decisive role in their realization. Clinical or medically-relevant measurements will demonstrate their viability, thus providing three incisive examples in which micro-optics and micro/nanosystems can play a significant role in modern medicine and environmental monitoring.

BIOGRAPHY

Hans Zappe was born in Paris and raised in New York. He earned Bachelor's and Master's degrees at MIT in 1983 and a PhD from the University of California, Berkeley, in 1989, all in Electrical Engineering.

His early research activities in electronics, integrated optics and semiconductor lasers took place at IBM (USA), the Fraunhofer Institute for Applied Solid State Physics (Germany) and the Centre Suisse d'Electronique et de Microtechnique (Switzerland). He joined the University of Freiburg in 2000, where he is now the Gisela and Erwin Sick Professor of Micro-optics in the Department of Microsystems Engineering.

With a strong focus on the development of novel micro-optical components and systems, his current research interests include tunable micro-optics, photonics for medical applications and printable integrated optics. In addition, he was Dean of Studies from 2002 to 2008 and Dean of Engineering from 2008 to 2010, and currently serves on the Board of Directors of the University Medical Center Freiburg.

Prof. Zappe founded and managed the DFG Priority Program "Active Micro-optics", and is co-founder and co-manager of the DFG Collaborative Research Center "Planar Optronic Systems". He has been general chairman of numerous international conferences, including IEEE MEMS and IEEE Optical MEMS and continues to serve on wide-ranging program and steering committees. He is editor of the Nature journals Light: Science and Applications and Microtechnology and Nanoengineer-



ing; senior editor of the IEEE Journal of Microelectromechanical Systems; and associate editor of the SPIE Journal Microlithography, Microfabrication, and Microsystems.

Microfluidic Orgain-on-a-Chip Platform

Noo Li Jeon, Ph.D.

School of Mechanical and Aerospace Engineering Seoul National University, Seoul 151-744, Korea E-mail: njeon@snu.ac.kr

There are numerous reports of *in vitro* experimental systems developed to investigate vessel dynamics and function, and for high-throughput screening, high-resolution imaging and experimental manipulation.¹ ECs cultured on 2D substrates are widely used for the investigation of barrier function, mechanosensitive response of endothelium, and transendothelial migration of blood-borne cells including leukocytes and circulating tumor cells (CTCs). However, such 2D monolayer-based systems lack three-dimensional contexts important for the native architectures and functions of blood vessels.

In contrast, three-dimensional extracellular matrices (ECMs) can provide an enhanced environment for multicellular organization of ECs as well as cell-cell and cell-matrix interactions, all of which have been shown to be critical in endothelial morphogenesis and function⁵. Unfortunately, to date, 3D *in vitro* assays have not provided a robust experimental method to grow readily perfusable blood vessels, precluding their use in experiments requiring delivery of small molecules, soluble proteins, cells or fluid flow-induced mechanical stimuli to the luminal surface of the endothelium. For instance, recent reports demonstrated *in vitro* vessel analogues made by endothelialization of channel-molded hydrogels or microfluidic channels to mimic cell migration, inflammatory response, and thrombosis under defined biomolecular and mechanical stimulations. Unfortunately, as the vessels did not follow natural developmental morphogenic process in making the lumenized structure, they were limited in their ability to reconstitute the natural features and responses.

Here we report a novel microfluidic platform and robust approach to form perfusable and functional microvascular networks in 3D ECM construct. The approach uses flexibly designed cellular co-culture to form microvascular networks and angiogenic sprouts, which facilitates controlled heterotypic cell-cell interactions and recapitulates natural morphogenesis of ECs observed *in vivo*. The open, unobstructed 3D microvascular networks engineered using this platform can form the basis of vascularized micro-organs for tissue engineering and drug discovery applications.

References

[1] Huh D., Matthews B. D., Mammoto A., Montoya-Zavala M., Hsin H. Y. and Ingber D. E.. "Reconstituting Organ-Level Lung Functions on a Chip". Science 328, 1662-1668 (2010)

Biography



Noo Li Jeon is a Professor of School of Mechanical and Aerospace Engineering at Seoul National University (SNU). He studied Materials Science and Engineering at Northwestern University (B.S.) and University of Illinois Urbana-Champagne (Ph.D.). He worked on soft lithography applications in Prof G.M. Whitesides' laboratory at Harvard University and at Prof M. Toner's group at Harvard Medical School. He was an Associate Professor at UC Irvine from 2001-2009 in the Biomedical Engineering Department. In 2009, he moved to Seoul National University to join School of Mechanical Engineering and WCU Program in Multiscale Mechanical Design at Seoul National University.

Mathematics & Informatics for Quantitative Biology

Tetsuya J. Kobayashi, Ph.D.^{1,2}

 ¹ Institute of Industrial Science, The University of Tokyo, Tokyo, Japan
 ² PRESTO Project, Japan Science and Technology Agency (JST), Japan. E-mail: tetsuya@mail.crmind.net

Modern biology has remarkably changed in the last two decades after the emergence of new innovative technologies. The development of bioimaging technologies enables us to quantitatively observe dynamic and complex biological phenomena at single-cell and even at molecular-level. The revolutionary and competitive development race of the next generation sequencing (NGS) technologies, on the other hand, has made it possible to obtain genetic and epigenetic information on thousands of genes by one experiment not only at population level but also at single-cell level. These new technologies now generate huge amount of quantitative big data that is far beyond our ability to manually and visually inspect the relevant information contained in the data.

Informatics and mathematics are indispensable for appropriately and effectively handling these data. Informatics, for example, provides us with the series of useful tools and platforms to automatically and effectively process, analyze and visualize the quantitative big data. Mathematics, in contrast, gives us the rigorous language to describe the rules behind the complex dynamics of biological phenomena inferred from the data. Integrating mathematics and informatics with biology is, therefore, becoming more and more important to quantitatively analyze, understand, predict, and control biological phenomena.

In this talk, I illustrate these roles of mathematics and informatics in biology. Specifically, I am going to show how image analysis, statistics, and mathematical modeling can be used in biology by picking up topics from immunology, embryogenesis and evolution as illustrative examples.

References

[1] R. Phillips, J. Kondev, J. Theriot; Physical Biology of the Cell. Garland Science (2012).

- [2] R. Milo, R. Phillips: Cell Biology by the Numbers. Garland Science (2016)
- [3] W. Bialek: Biophysics: Searching for Principles. Princeton University Press (2012).
- [4] T.J. Kobayashi, Y. Sughiyama: Fluctuation Relations of Fitness and Information in Population Dynamics. Phys. Rev. Lett. 115(23), 238102 (2015)
- [5] T. Akiyama, R. Tateishi, N. Akiyama, R. Yoshinaga, T. J. Kobayashi: Positive and negative regulatory mechanisms for fine-tuning cellularity and functions of medullary thymic epithelial cells. Front. Immunol. 6, 461 (2015).
- [6] Md. K. Bashar, K. Yamagata, T. J. Kobayashi: Improved and Robust Detection of Cell Nuclei from Four Dimensional Fluorescence Images. Plos One, 9(7), e101891 (2014).

Biography



- **2000**: B.S. Engineering, the University of Tokyo.
- 2002: M.A. Engineering, the University of Tokyo.
- 2005: Ph.D. Science, the University of Tokyo.
- 2002–2005: JSPS Doctoral Course Research Fellow @ Univ. Tokyo, Japan.
- 2005–2008:JSPS Postdoctoral Research Fellow @ Center for Developmental Biology(CDB) RIKEN, Japan.
 - 2008 RIKEN Special Postdoctoral Researchers (SPDR) @ CDB, Japan.
- 2008–2011: Lecturer, Institute of Industrial Science, Univ. Tokyo, Japan.
- **2011–present**: Associate Professor, Institute of Industrial Science, Univ. Tokyo, Japan.
- 2009–2013 & 2015–present: Project Researcher, Precursory Research for Embryonic Science and Technology (PRESTO), JST, Japan.

Processes and characterization tools for low temperature wafer-level vacuum packaging

Alain Bosseboeuf

Center for Nanoscience end Nanotechnology (C2N), CNRS, University Paris Saclay, Univ Paris Sud,

91405 Orsay, France E-mail: alain.bosseboeuf@u-psud.fr

Vacuum packaging is mandatory for some devices to get high performances. This is the case for mechanical resonant sensors (suppression of air damping), thermal sensors (reduction of thermal losses) and for various other devices like optical scanners, microswitches and for some energy harvesters and microfluidic devices. Achievement of wafer-level vacuum packaging with state of the art performances is a very challenging task: it notably requires low temperature hermetic bonding with very low outgassing and leak rates as well as getter films with low activation temperature and high sorption capacity. In this lecture, after a brief overview of basics of vacuum wafer-level packaging, transient liquid phase wafer bonding and multilayer getter film investigated at C2N to get low temperature wafer-level vacuum vacuum packaging will be presented. Numerous characterization techniques must be used for these investigations and some specific techniques that we have developped will be illustrated by recent results.

References

[1] M. Wu, J. Moulin, S. Lani, G. Hallais, C. Renrad, A. Bosseboeuf, *Low temperature activation of Au/Ti* getter film for application to wafer-level vacuum packaging. Jap. J. Appl. Phys., vol. 54, p. 030220, 6 pages, (2015)

[2] S. Lemettre, S. Seok, N. Isac, J. Moulin, A. Bosseboeuf, BOSSEBOEUF A. Low temperature solid–liquid interdiffusion wafer and die bonding based on PVD thin Sn/Cu films. Microsystem Technologies, p.1-7 (2016)

[3] S. Lemettre, S. Perrot, S. Seok, N. Isac, J. Moulin, A. Bosseboeuf, *Hermeticity characterization of low temperature SLID bonded packaging using thin PVD Cu/Sn metallization*. Conference on wafer bonding for microsystems, 3D and wafer level integration (Waferbond 2015), Braunschweig, Germany, 8-9 Dec (2015)

[4] M. Wu, D. Mansour, M.-P. Plante, A. Bosseboeuf, S. Seok, J. Moulin, *Evaporated Zr-V, Zr-Ti and Zr-Co getter thin films: Activation temperature and microstructure*. Symposium on Design, test, Integration and Packaging of MEMS/MOEMS (DTIP), Budapest, Hungary May30-June 2, (2016)

[5] M. Wu, J. Moulin, P. Coste, S. Perrot, J.-L. Perrossier, A. Bosseboeuf, *Comparative study of Au/Ti, Au/V, and Au/Zr films gettering ability for application to wafer-level vacuum packaging*, 26th Micromechanics and Microsystems Europe workshop, Toledo, Spain, 20-23 September 2015

Biography



Alain Bosseboeuf obtained in France a master degree in microelectronics from INPG, a telecommunications engineer diploma from ENSTBr in 1980 and a master degree in Solid State Physics from University Paris 6 in 1981. He received the PhD degree in Physics from University Paris South (Orsay) in 1989. In 1983-2016 he works as a CNRS full-time researcher in the Institut d'Electronique Fondamentale (IEF), a joint institute of CNRS and University Paris South located in Orsay (France). Since June 2016, he is researcher in Centre de Nanosciences and Nanotechnologies (C2N) in University Paris Saclay /CNRS-University Paris Sud. After more than 10 years of research activity on thin film deposition and characterization, he started to work in the field of microsensors and MEMS at the beginning of nineties. He has led the research

group "NanoBio and Micro/nanosystems" of IEF and the CIRMM/CNRS-Unisersity of Tokyo Paris office for 10 years. Since November 2005, he is also coordinating the international research network NAMIS (Nano and Microsystems) involving 12 partners from 10 countries. His current interests include resonant sensors; MOEMS; wafer bonding, getter films and measurement techniques for wafer level packaging and 3D integration; and thin film materials and technology for physical microsensors. He is co-author of more than 160 papers in International journal or conferences.

Microfluidics for hepatic tissue engineering: New 3D cell-culture approaches using microfibers and microparticles produced by microfluidic technologies

Masumi Yamada, Ph.D.

Department of Applied Chemistry and Biotechnology, Chiba University, Chiba, Japan E-mail: m-yamada@faculty.chiba-u.jp

Isolated hepatocytes from the liver are highly important as they are used for numerous biomedical applications, including cell-based drug screening assays and cytotoxicity testing of chemicals. However, hepatocytes easily lose their differentiated functionalities when they are cultured *in vitro*, primary because of the difference with the *in vivo* environments in terms of (i) 3D cell arrangement, (ii) heterotypic/homotypic cell-cell interactions, and (iii) presence of proper ECM components. Researchers have proposed various methods to reconstruct these factors *in vitro*, but effective strategies are still under development. In recent years, microfluidic devices have been utilized to prepare micrometer-size objects such as particles [1, 2] and fibers [3, 4]. In this lecture, we will briefly introduce our recent research progresses on two topics; (1) coculture of hepatocytes and non-parenchymal cells in hydrogel microfibers/microsheets and (2) formation of composite multicellular spheroids encapsulating collagen microparticles.

As a first approach, sandwich-type anisotropic hydrogel microfibers, encapsulating hepatocytes in the center and non-parenchymal cells (3T3 cells) on both sides, were produced using microfluidic devices [5]. We confirmed that complex, linear microorganoids composed of hepatocytes and 3T3 cells were formed within the hydrogel matrix of the fiber. The hepatic functions were maintained for a long time period (~60 days) mainly because of the formation of proper cell-cell interactions in a 3D manner, as in the case of the *in vivo* liver tissues. In addition, we were able to produce hydrogel sheets for parallel formation of complex microorganoids [6]. The current approach was considered to be highly advantageous for conducting hepatocyte-based drug-screening applications and constructing bio-artificial liver models.

Next we proposed a technique to produced cell-sized, highly condensed collagen microparticles using microfluidic devices or membrane emulsification [7]. Droplets of an aqueous solution of type I collagen were generated in a continuous phase of a polar organic solvent (ex. methyl acetate). The formed droplets rapidly shrunk because of dissolution of water molecules into the solvent. After shrinkage, condensation, and chemical closslinking, collagen microparticles with sizes of several micrometers were obtianed. We prepared composite multicellular spheroids of hepatocytes incorporating collagen microparticles by introducing them in non-cell-adhesive microwells. Hepatocyte-specific functions were upregulated when collagen particles were added at a proper ratio, mainly because of the formation of cell-ECM and cell-cell interactions. We consider that these studies were good examples of applying micrometer-sized materials, produced by using microfluidic devices, to hepatic tissue engineering.

References

[1] S. Sugaya, et al., *Biomicrofluidics*, 7, 054120 (2013); [2] M. Mizuno, et al., *Langmuir*, 31, 2334 (2015); [3] M. Yamada, et al., *Soft Matter*, 8, 3122 (2012); [4] Y. Kitagawa, et al., *Biofabrication*, 6, 035011 (2014); [5] M. Yamada, et al., *Biomaterials*, 33, 8304 (2012); [6] A. Kobayashi, et al., *J. Biosci. Bioeng.*, 116, 761 (2013); [7] M. Yamada, al., *Lab Chip*, 15, 3941 (2015).

Biography



Dr. Masumi Yamada graduated from Department of Chemistry and Biotechnology, School of Engineering, University of Tokyo in 2001 and obtained Ph.D. (Engineering) in 2006. Then he worked as a postdoctoral researcher in Tokyo Women's Medical University (2006-2008, with Prof. Teruo Okano) and in Massachusetts Institute of Technology (2008-2009, with Prof. Jongyoon Han). He moved to Chiba University as an Assistant Professor in 2009, and from 2013 he is working as an Associate Professor. His research interests include microfluidic systems and technologies for developing new tools for chemistry, biotechnology, and tissue engineering.

Lecture (I)

The NAMIS international network: a short overview

Alain Bosseboeuf

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The NAMIS (Nano and Micro Systems) international research network was founded in Nov 2005 and is now gathering 12 partners from 10 countries: Centre National de la Recherche Scientifique (CNRS) (France), IIS/The University of Tokyo (Japan), Ecole Polytechnique Fédérale de Lausanne (EPFL)(Switzerland), IMTEK/ University of Freiburg (Germany), VTT Ltd (Finland), Seoul National University (SNU)(South Korea), Polytechnique Montréal (Canada), Korea Institute of Machinery and Materials (KIMM) (South Korea), University of Washington (USA), University Paris Est (France), National Tsing Hua University (NTHU) (Taiwan), MESA+/University of Twente (The Netherlands). It represents more than 80 laboratories/research groups. The NAMIS network already organized 14 workshops all around the world and 9 international schools. At NAMIS school in Tokyo, Research topics, benefits for students /post-docs, website and other useful information will be summarized and announcement of future NAMIS workshops and schools will be done. Regularly updated information on NAMIS network can be found in website http://namis.iis.u-tokyo.ac.jp.

Biography



Alain Bosseboeuf obtained in France a master degree in microelectronics from INPG, a telecommunications engineer diploma from ENSTBr in 1980 and a master degree in Solid State Physics from University Paris 6 in 1981. He received the PhD degree in Physics from University Paris South (Orsay) in 1989. In 1983-2016 he works as a CNRS full-time researcher in the Institut d'Electronique Fondamentale (IEF), a joint institute of CNRS and University Paris South located in Orsay (France). Since June 2016 he is researcher in Centre de Nanosciences and Nanotechnologies (C2N) in University Paris Saclay /CNRS-University Paris Sud. After more than 10 years of research activity on thin film deposition and characterization, he started to work in the field of microsensors and MEMS at the beginning of nineties. He has led the research

group "NanoBio and Micro/nanosystems" of IEF and the CIRMM/CNRS-Unisersity of Tokyo Paris office for 10 years. Since November 2005, he is also coordinating the international research network NAMIS (Nano and Microsystems) involving 12 partners from 10 countries. His current interests include resonant sensors; MOEMS; wafer bonding, getter films and measurement techniques for wafer level packaging and 3D integration; and thin film materials and technology for physical microsensors. He is co-author of more than 160 papers in International journal or conferences.

9:15 - 10:00, Wednesday, 14th Sep., 2016

Optical Microresonators

Yves-Alain Peter, Dr. ès Sc.

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On chip optical microresonators [1, 2] are compact, robust and can be integrated with micro electro-mechanical components as well as microfuidics. They can efficiently sense acceleration [3], forces [4], gases [5], refractive index of liquids [6] and living cells [7, 8], and bacteria [9].

During the seminar I will give an overview of projects exploiting this new avenue (sensors and tunable devices based on different types of optical microresonators). In-plane Fabry-Pérot microcavities integrated on chip will be specifically highlighted through several different applications.





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Biography



Yves-Alain Peter received the M.Sc. degree in physics and the Dr.Sc. degree from the University of Neucha^{*}tel, Switzerland, in 1994 and 2001, respectively. In 1995, he joined the Department of Medical Radiobiology as a Research Associate at the Paul Scherrer Institute, Switzerland. From 1995 to 2001, he was a Graduate Research Assistant with the Applied Optics Group, Institute of Microtechnology, University of Neucha^{*}tel. From 2001 to 2003, he was a Post-Doctoral Researcher with the Microphotonics Group, Stanford University. From 2003 to 2004, he was a Research and Development Engineer and a Project Leader with the Swiss Center for Electronics and Microtechnology, Switzerland. In 2004, he joined Polytechnique Montre^{*}al, Canada, where he is now Professor of Engineering Physics. His current research interests include microphotonics and micro-opto-electro- mechanical systems.

Integrated bio-functionalization techniques in fluidic MEMS: How to play with magnetic nanoparticles for immuno-assays

Mehdi AMMAR, Ph.D. Centre for Nanoscience and Nanotechnology – C2N Université Paris Sud, CNRS, Orsay, France Tel : +33 1 69 15 39 70 E-mail : mehdi.ammar@u-psud.fr

The lecture will present an approach of innovative BIOMEMS dedicated to an ultra-sensitive and controlled protein detection. The concept is based on a fully-integrated immune-complex assays [antibody – biomarker – antibody – fluorescent dye and/or magnetic nanoparticles] inside microfluidic systems. The first part of the lecture will be focused on the presentation of high efficient techniques of dynamic functionalization (silanization) of silicon microchannel with carboxylic or amine functions, while forming a monolayer which can accept protein and recognize specific biomarkers of neurodegenerative diseases or for bacteria detection. To attain a very high performance of dynamic silanization, the internal surface of the microchannel is systematically characterized by XPS, AFM and FTIR to optimize several parameters of the silanization method (temperature, solvent, flow rate...).

The second part of the lecture is relied on the bio-functionalization of magnetic nanoparticles by controlling their movement within integrated microcoils in fluidic microsystems. The trapping of immune-functionalized nanoparticles offers several advantages such as (i) the control of multi-level immune-complex construction (ii) the possibility, as captured element, to concentrate the biomarkers of interest from a complex biological sample, (iii) by applying a magnetic field, the nanoparticles will be concentrated in the detection area and the kinetic of the immunologic recognition will increase (iv) their detection by the electromagnetic signal collected by the microcoils could be considered as an original alternative to the fluorescence technique. The presented biosensing concepts are applied to the sensitive detection of Alzheimer disease biomarkers (Amyloid peptides, Tau protein, ERK1/2) or cardiac pathologies (BNP, Troponin I biomarkers) or recently for bacteria detection.

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Biography



Dr. Mehdi AMMAR is a researcher at the "Center for Nanoscience and Nanotechnology" from University Paris Sud and CNRS (previously IEF). He received his M.S. degrees in Nanostructures and Nanotechnologies from University Paris Sud and his Ph.D in Physics, in the field of nanostructured magnetic materials, in 2007 from ENS Cachan. His research interests cover micro/nanotechnologies, surface bio-functionalization and characterization techniques, in particular for the development of specific physical and biochemical micro-sensors. For a few years, his activity focused on developing controlled coating techniques of nanostructured materials in particular magnetic nanoparticles (sol-gel techniques). Since 2009, he has developed activities in the topic of dynamic bio-functionalization techniques in fluidic microchips using magnetic nanoparticles for bioanalysis applications (in particular Alzheimer biomarkers detection). Current focus is the field of bacteriological detection for biodefense applications.

Towards Atomic Force Microscopy with Real Time Mapping of Morse Parameters

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It is of great importance to establish a robust and versatile method to map the chemical species or states with atomic resolution. Such functions can be found in high resolution TEM, Atom Probe Microscopy, and High resolution Optical spectroscopy. Force spectroscopy utilising Atomic Force Microscopy also holds great possibilities in implementing such functions [1,2]. Here we introduce a method of control and data treatment that enable real time acquisition of the Morse parameters of the potential field defined by the tip and the sample. The sample is position modulated in the tip sample direction at frequency ω , and a lock in amplifier used to detect the gradient of the frequency shift (df) curve (FC) of the cantilever self-excitation. Tip sample distance is regulated so that the 1 ω component of df is kept at zero. We call this method "Bottom Tracking" for short, since the bottom of the frequency shift curve becomes the working point at low dither amplitudes. Using the formula that gives the frequency shift df from a given potential, and by using the working point maintained by Bottom tracking as the boundary condition, one can calculate the three Morse parameters for a given FC. In actual operation, the DC component and the 2ω components of df and the regulated movement of the z piezo element Zd0 are used to calculate the Morse parameters. Figure 1 shows an example of such image acquisition performed on quenched Si(111). It was demonstrated that Bottom Tracking gives atomic resolution on Silicon and solder. By assigning the three Morse Parameters to RGB values to form an image, one can obtain an image in colour, where sites with different set of Morse parameters are displayed with a different colour. For example, sites A and B are more or less identical in the topographic image(ZD0), but show distinctly different colours when expressed in terms of RGB. The calculated Morse parameters are in reality, only "effective" Morse parameters since the FC is under the influence of various background forces as well as the state of the tip apex.

For example, mesoscopic tip volume would change the contribution of Van der Waals Force, and hence change the apparent value of potential minima. That admitting, the method does have the capability to present something different as being so. In order to make this a reliable and quantitative method, further study is needed to define a reference tip and to clarify the protocol to assure repeatability of the imaging technique.

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Fig.1. An example of Morse Parameters calculated from measured values during Bottom Tracking. Sample quenched Si(111). Scan 3x3 nm.



Hideki Kawakatsu, Professor, UTokyo 1990~ present

1995~1997 Visiting Professor at the Institute for Physics, Uni Basel, Switzerland and LPMO/CNRS Besançon, France.

2014.9~ Co-director of LIMMS (CNRS/IIS), 2016.4~ Director of CIRMM

Nonlinear Nanoelectrokinetic Ion Concentration Polarization and its Energy/Environmental/Bio Applications

Professor Sung Jae Kim, Ph.D.

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Ion Concentration Polarization (ICP) phenomenon is traditional electrochemical ion transportation process and appears as a steep concentration gradient near nanoporous membrane under dc bias[1]. The major function of ICP is an active ion control by an external electric field so that it is significantly useful to study the new ion transportation through nanoporous junction (or membrane)[2-4]. The lecture would mainly focus on the physics of ICP and introduce novel engineering applications such as high energy efficient purification system,[5-7] bio-sample selective preconcentrator[8-10] and ionic field effect transistors[11, 12]. Problems behind these applications such as instability[13] will be also discussed.



Figure. The demonstrations of (a) enhancing energy efficiency of electrochemical membrane using external hydrodynamic inflow[2], (b) selective preconcentration of biomolecules[9] and (c) suppressing instability in micro-confinement[3].

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Biography



Professor Sung Jae Kim received the B.S. and M.S. degree in department of Chemical Engineering of Pohang University of Science and Technology, Pohang, Korea, in 1998 and 2000, respectively. He received his Ph.D. from department of Chemical Engineering and division of Mechanical and Industrial Engineering from the same university in 2005. He joined MIT as a postdoctoral associate in December 2005 and he continued to work as Research Scientist at the same group in MIT. From 2012, he joined Seoul National University as an assistant professor at Department of Electrical and Computer Engineering and promoted to an associate professor in 2016. His current research program focuses to the fundamental nanoscale electrokinetics especially ion concentration polarization phenomenon and its engineering application in the field of energy, environment and bio sector.

Dissoluble Microneedle patch for transdermal drug delivery systems

Beomjoon KIM, Ph.D., Professor

CIRMM, Institute of Industrial Science, The University of Tokyo, Tokyo, Japan E-mail: bjoonkim@iis.u-tokyo.ac.jp

Our research goals are to build smart nanosystems and integrate nanoscale components in micro sensors, in particular for environment, bio-sensing, through both bottom-up and top-down approaches. We focus on interdisciplinary research about local "bottom-up" surface modification using functional self-assembled monolayers and "top-down" approaches for micro/nano patterning technologies. Based on these studies on nano/micro components systems for the fabrication of novel nano devices, we investigate to develop various micro sensors for biological applications, health care as well as environmental monitoring. Moreover, we are interested to develop self-powered, energy harvesting micro sensors as well as smart monitoring system with network like "internet of things", "Trillion sensors universe".

In this lecture, new transdermal drug delivery system by using dissoluble micro needle patch will be introduced.

The transdermal drug delivery has experienced several-generation revolutions: From the transdermal delivery of small, lipophilic, low-dose drug to the delivery system using chemical enhancer, non-cavitational ultrasound and iontophoresis. With the development of the micro-scale engineering, microneedles show the potential to be the next generation delivery system. The microneedle mediated drug delivery system has been developed to provide painless self-administration of biological drug with patient friendly manner. Especially, dissolving microneedles, which deliver the target drugs as the drug-loaded microneedle dissolves into the skin, have been spotlighted recently. We investigate a novel fabrication method to achieve the user-friendliest, low-cost, and safest way for dissoluble microneedle patches with vaccine delivery.



Biography



He received the B.S. degree from Seoul National University, Dept. of Mechanical Design and Production Engineering, Seoul, Korea, in 1993, and received M.Eng., and Ph.D. in Department of Precision Engineering, the University of Tokyo, Tokyo, Japan, in 1995 and 1998, respectively.

He is currently a Professor of Institute of Industrial Science, the University of Tokyo, Japan (since April. 2014). (Dept. of Precision Engineering, The Univ. of Tokyo)

From 1998 to 1999, he was a CNRS Associate Researcher for Microsensors, Nanoinstruments for Nanotechnology in Centre National de la Recherché Scientifique (CNRS) / Laboratoire de Physique et Metrologie des Oscillateurs (LPMO) at Besancon, France. He worked also in research orientation NanoLink, MESA+ Research Institute, University of Twente in the Netherlands, to September 2000. Since September 2000, he has been an associate professor of Institute of Industrial Science, the University of Tokyo until 15. April 2014.

He has been a co-director of CIRMM/CNRS Paris office, since 2001 for 3 years to coordinate collaborations with other European countries in MEMS/NEMS research.

Dielectrophoresis and magnetophoresis integration and applications in microfluidic devices

Rosaria Ferrigno

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Cells at very low concentration, typically less than 1000 target cells per milliliter of body fluids, are considered as circulating rare cells or low-abundance cells. A typical example is Circulating Tumor Cells (CTCs) that are at a concentration as low as 1 to 100 CTCs/mL of peripheral blood from a human cancer patient. Enumeration of such rare cells presents medically important applications such as in cancer diagnosis and prognosis, non-invasive prenatal diagnosis and cell-based therapies. Therefore, there is a tremendous challenge[1] in the development of technologies and devices able to manipulate, enrich, capture, separate them from a sample containing a large amount of other cells. Such technologies must demonstrate high purity and recovery rate while keeping the cells intact for downstream analyses.

Two main approaches, affinity-based[2] and label-free[3] methods, have already been demonstrated in microfluidic format. For both approaches, the use of field gradient, electrical field for dielectrophoresis (DEP) and magnetic field for immuno-magnetic separations, has gained a large interest[4]. However, to be applied to real clinical samples and become commercial products, these devices and methodologies still need development.

This lecture is designed as an introduction to the integration of these two strategies in microfluidic devices. After presenting the general theoretical concepts, the author will first focus on the technological aspects. Indeed, the generation of controlled field gradient in microfluidic format necessitates the integration of heterogeneous materials. Although most of the microfluidic systems are fabricated in polymer materials, microsystems integrating active functions - requiring the generation of either magnetic or electric field gradients - necessitates the integration of metallic materials in these polymers. Different approaches can be used and among them, the author will show the use of composite polymers developed in her group. It has been shown that the integration of 3D microstructures can improve active function performances. However, 3D microstructure fabrication and integration are more challenging than conventional 2D coplanar patterns.

Then, application of DEP and magnetophoretic approaches for separation, capture and manipulation of biological cells will be highlighted.

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Biography



Rosaria Ferrigno received the Ph.D. degree in electrochemistry from the Swiss Federal Institute of Lausanne, Lausanne, Switzerland, in 1998. From 2000 to 2003, she was a Postdoctoral Fellow at Harvard University, Cambridge, MA, in the group of Prof. Georges M. Whitesides, where she worked on integrating electrochemistry in microfluidic devices. Since 2003, she has been Professor with the Electrical Engineering Department, University Claude Bernard of Lyon, France, where she is involved in the development of lab-on-chip and microfluidic devices applied to analytical chemistry and biology.

Circuit and System Design for Organic Electronics

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The organic electronics enables flexible, large-area, and distributed sensor and/or actuator array and is suitable for the wearing-unconscious devices used in biomedical and healthcare applications. The circuit design in the organic electronics, however, differs from the conventional CMOS circuit design for silicon VLSI, because organic transistors often show large within-die and die-to-die variations and a drift of the transistor characteristics over time. In some cases, CMOS circuit design is not available, because nMOSFETs are often unavailable in the organic electronics. To solve the design challenges, new circuit and system design techniques for the organic electronics are required. In this talk, the circuit and system design solutions combined with new device technologies for the organic electronics are reviewed.

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Biography



Makoto Takamiya received the B.S., M.S., and Ph.D. degrees in electronic engineering from the University of Tokyo, Japan, in 1995, 1997, and 2000, respectively. In 2000, he joined NEC Corporation, Japan, where he was engaged in the circuit design of high-speed digital LSI's. In 2005, he joined University of Tokyo, Japan, where he is an associate professor of VLSI Design and Education Center. From 2013 to 2014, he stayed at University of California, Berkeley as a visiting scholar. His research interests include the design of low-power RF circuits, ultra low-voltage logic circuits, low-voltage power management circuits, and large-area and flexible electronics with organic transistors. He is a member of the technical program committee of IEEE International Solid-State Circuits Conference and IEEE Symposium on VLSI Circuits. He received 2009 and 2010 IEEE Paul Rappaport Awards and the best paper award in 2013 IEEE Wireless Power Transfer Conference.

TEM: Atomic Resolution Microscopy and Spectroscopy

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Transmission electron microscopy (TEM) is a microscopy using electron, and very high spatial resolution can be achieved with TEM. Especially, with the grace of a spherical aberration (Cs) corrector for an electromagnetic lens, the spatial resolution of the TEM has been dramatically improved, like 0.48Å (0.048nm). Highly convergent electron is used in scanning TEM (STEM). By selecting the collection angle of the transmitted electron for the image, we can obtain some fruitful information. For instance, the image generated only by thermal diffuse scattering (TDS) provides atomic number (Z) related information. Namely, the image contrast is approximately proportional to the square of the atomic number (Z). Such imaging mode is called high angular annular dark field (HAADF) image. This HAADF image is suitable to visualize the heavy elements. In contrast, by using smaller annular type detector, we can obtain annular bright field (ABF) image, which can visualize light elements, even hydrogen. STEM is powerful because both ABF and HAADF can be simultaneously observed. Namely, by using HAADF and ABF, we can identify most of all elements (column..) in the Periodic table.

In addition to the imaging, a very powerful spectroscopic analysis can be performed using TEM. Since one can make very small electron prove, <0.5Å, a spectrum from (in principle) a single atomic column can be observed. X-Ray Energy dispersive spectroscopy (EDS/EDX) is mainly used for the chemical analysis. Large-size detector was been developed recently, we can obtain the atomic resolution chemical mapping using the STEM-EDS. Electron energy loss spectroscopy (EELS) is one of the most powerful spectroscopy method, because multiple information, such as atomic structure, band structure, composition, and bonding information, can be obtained with the atomic resolution.

Recently, my group is doing atomic resolution analysis of amorphous materials, liquid, and gas. In my lecture, I will introduce the basics and some applications of TEM and EELS.

Biography



Teruyasu Mizoguchi is an associate professor in Institute of Industrial Science, University of Tokyo. He received PhD from Kyoto University in 2002, dealing with experimental and theoretical X-ray Absorption Fine Structures (XAFS). From 2002~2005, he has been a postdoctoral researcher at Kyoto University, University of Tokyo, and Lawrence Berkeley National Laboratory, focusing on the atomic resolution investigation of materials. He became a research assistant in 2005 and an assistant professor in 2007 in Institute of Engineering Innovation, University of Tokyo. He moved to the present position in Dec. 2009. His research interest is development and application of theoretical EELS, atomic resolution analysis of glass, liquid, and gas. Currently, he is also working on materials informatics.

Micro/nanofluidics-based sustainable energy harvesting using electrokinetic effects: recent advances and remaining challenges

Laurent Joly

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Sustainable energy harvesting is one of the greatest challenges of our society, to which micro and nanofluidics offer promising solutions. For instance, nanofluidic membranes based on boron nitride nanotubes can harvest the "blue energy" (the osmotic energy of salt water) with unprecedented efficiency [1]. Micro/nanofluidic devices could similarly be used to harvest waste heat, although this possibility has hardly been explored so far. At the core of fluidic energy conversion lie electrokinetic (EK) effects, which cover all possible couplings between different types of transport, i.e. when a thermodynamic gradient of one kind induces a flux of another kind. The most used and studied EK effects couple hydrodynamic and electrical transport: electro-osmosis – flow induced by a gradient of electric potential – and streaming current – electric current induced by a pressure gradient. Similarly, a gradient of salt concentration can induce an electric current, an effect recently used in blue energy systems [1]. A temperature gradient should also induce fluxes of different types, e.g. flows, electrical current, or salt current. These last EK effects could therefore be used to produce drinking water or electricity from waste heat.

During this lecture, I will first present the standard description of EK effects, focusing on the coupling between hydraulic and electrical energy through streaming current and electro-osmosis. I will then discuss the limits of this standard description, revealed by recent experiments and numerical simulations. I will in particular consider the role of interfacial hydrodynamics, of varying viscosity and dielectric permittivity close to the interfaces, and of ionic specificity toward surfaces. If I have time, I will illustrate this discussion with the example of EK effects in liquid foams, which could be used as cheap nanofluidic systems (so-called soft nanofluidics). I will finally extend the discussion to EK effects driven by osmotic and thermal gradients. I will then discuss the efficiency of energy conversion in micro and nanofluidic devices and in membrane-based systems, here again considering electricity production from both hydraulic and osmotic energy. I will in particular show how interfacial hydrodynamics can increase the efficiency of energy conversion. Finally, I will conclude by summarizing the challenges that remain to be addressed for the development of efficient micro and nanofluidic energy conversion systems.

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Biography



Laurent Joly is an assistant professor in the Institute of Light and Matter at the University of Lyon 1. He is working on nanofluidic transport, with particular focus on interfacial hydrodynamics and energy conversion using electrokinetic effects. To tackle these questions, he couples numerical modeling at different scales (from molecular modeling to finite elements) with analytical developments, in close interaction with experiments. He obtained a PhD in physics in 2005 from the University of Lyon 1. During his PhD, he combined experiments and numerical modeling to investigate the hydrodynamic boundary condition at the nanoscale, and its consequences on electrokinetic phenomena. He then worked as a postdoctoral researcher in a physical metallurgy lab at the French atomic energy commission. In 2006 he moved to the University of Lyon 1 and he has been working there since. In 2014, he was a visiting fellow at University College London, where he worked on ab initio modeling of liquid-solid friction.

"MEMS-de-Piano": a short turn-around-time experimental course in UTokyo Nanotechnology Platform

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Micro Electro Mechanical Systems (MEMS) is expected to be a key technology for sensing and actuation elements in nearly-coming Internet of Things (IoT) era. To educate skillful engineers is therefore highly demanded including university students and enterprises engineers. However, since MEMS technology spreads over different disciplines such as Electrical, Mechanical, Material engineering, it is difficult to really understand mems through classical discipline-based undergraduate courses. On the contrary, as they say "seeing is believing", designing MEMS actuators and observing them can tell many things to students. Based on the above mentioned consideration, the author gives an experimental course of "design, fabrication, and analyses of MEMS devices" since 2006[1]. The course is actually a full five days' course. In the end of course, an in-plane oscillating MEMS device is fabricated on a Silicon-on-Insulator (SOI) chip, by taking advantage of the UTokyo VDEC's supercleanroom environment, operated in collaboration with MEXT's National Nanotechnology Platfor Nanofabrication Project, including rapid direct writing Electron Beam (EB) machine and thick (1.2µm) EBeam resist. Its resonance to sinusoidal voltage input is measured by stroboscopic microscope and precisely analyzed. A simple linear vibration equation can precisely explain fabricated MEMS device's characterization.

In the beginning of the course, the design was rather "open" to students – students had a free-hand to design whatever they like; inspired by the University of Twente's presentation in the Micromechanics and Microengineering Europe Workshop (MME) 2010[2], the author decided to fix the target device as "resonator that oscillates at the requested frequency". It is since that time that the lecture theme is called "*MEMS-de-Piano*"; the word is actually in Japanese word that means "Piano by MEMS". Certain design have been found to reliably oscillate despite uncertainty of fabrication processes. In the NAMIS lecture, several "must-know" basic knowledges will be recalled through introduction of the experimental course.

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Biography



Dr. Yoshio MITA is an associate professor of the Department of Electrical and Electronics Engineering, the University of Tokyo. Since 2012, Dr. Mita also serves as MEXT's Nanotechnology Platform University of Tokyo VDEC site manager. He got his Bachelor, Master, and Ph.D degrees of Electrical Engineering from the University of Tokyo in 1995, 1997 and 2000, respectively. After his PhD, he served as an assistant professor of VLSI Design and Education Center (VDEC), and was promoted to Lecturer at the Department of Electrical Engineering in 2001 and then to Associate Professor in 2005. In June 2013 Dr. Mita was prized "Best Teaching Award" by Faculty of Engineering of U.Tokyo for his lecture of Electro-Informatic Systems.

Technology of far-infrared detectors and sub-THz cameras at VTT Technical Research Centre of Finland

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Sub-mm wave imaging at 0.1-1 THz is a novel solution for security screening of concealed objects in mass transit areas, requiring real-time multi-band imaging systems with high radiometric and spatial resolution at diffraction limit. For the last decade VTT has developed sub-mm wave superconducting bridge and kinetic inductance bolometer technologies and demonstrated large format 2D imaging focal plane array camera prototypes. We review the current status of the detectors and sub-THz camera technologies and discuss future improvements of system performance. The lecture also covers recent VTT developments on far-infrared graphene field electron transistors and semiconducting thermal detectors. Trade-off analysis of camera performance and challenging engineering issues are considered.

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Biography



Andrey Timofeev received MSc in physics in 2004 from Lomonosov Moscow State University, carrying out diploma work on superconducting – weak ferromagnet Josephson π -junction devices. He received PhD degree in 2009 from Low Temperature Laboratory, Helsinki University of Technology, performing sub-Kelvin measurements on shot noise statistics and heat transport in mesoscopic superconducting tunnel junction circuits at the quantum limit. In 2009 he joined VTT Quantronics team to develop superconducting sub-THz detectors and cameras technology for stand-off security imaging. He developed rf-multiplexed kinetic inductance bolometer technology and built large focal plane array camera modules within his Finnish Academy Post-Doctoral Fellowship 2011-2013 and EU Consortis project 2014-2017. In 2014 he also joined VTT Nano-electronics team to develop nano-thermocouple detectors for IR and THz applications.

Throughout his career at VTT he has also conducted feasibility studies, microfabrication and experiments on Coulomb blockade primary thermometers, superconductor/normal metal/semiconductor microcoolers, silicon waveguide integration with superconducting single photon detectors, and plasma-wave graphene FET THz detectors. His research interests also include solid-state qubits and quantum computation. He has 2 patent applications on thermal detectors and 20 peer-reviewed publications.

Poster List

Group Number	Last name	First name	Affiliation	Poster title
G1-01	Chikamori	Masatomo	IIS	Microfluidic devices for Applying shear stress to primary cilia on on Tubular cells
G1-02	Martinez Santamaria	Jaime Andres	CNRS	Characterization of interdigitated electrodes for ECIS assys
G1-03	Bronuzzi	Jacopo	EPFL	Principle of Transient Current Technique for interfaces characterization in bonded silicon
G1-04	Descent	Philippe	EPM	Printing and integration of hybrid microsystems on flexible substrate
G1-05	Okumura	Shu	IIS	Multiplexed microRNA classidication by DNA computing
G1-06	Su	Meng	IIS	Self-powered hybrid sensor
G1-07	Hibi	Masashiro	IIS	Development of an Educational Atomic Force Microscope
G1-08	Gopi	Praveen Kumur	NTHU	Thermal stress redistribution by silicon surface nanostructure for high temperature applications
G1-09	Kim	Suryong	SNU	Fabrication of radical nano fiber using electro-spinning
G1-10	Timofeev	Andrey	VTT	Nanoelectronics, detectors and cameras technologies at VTT
G2-01	Takayama	Yuki	IIS	Investigating mechanical properties of Cancer Stem Cells (CSCs) vs non-CSCs usingmicromachined tools.
G2-02	Dassimu Diallo	Alpha	CNRS	Hybrid Diaphragm development for A MEMS based Stirling engine
G2-03	Lefebvre	Olivier	CNRS	Innovative methods for the integration of immunosensors based on magnetic nanoparticles in lab-on-chip
G2-04	Mikulik	Dmitry	EPFL	Realization of GaAs Nanowire based solar cells on Si substrate
G2-05	Sayed Herbawi	Abdalrah- man	IMTEK	High density CMOS-based neural probe with 32 parallel output lines
G2-06	Tajima	Hisatsugu	IIS	Control of dynamics of gene expressions by combining optogenetics and microfluidics
G2-07	Tan	Xinfeng	IIS	Measurement of Mechanical Properties of Nano-particles by Using AFM
G2-08	Hsiao	Yi-Hsing	NTHU	Affinity-based Sorting of Bacteriophages using a Gel Electro- microfluidic Chip
G2-09	Choi	Hansol	SNU	Diameter controllable DNA origami nanopore system
G2-10	Pernu	Таріо	VTT	Measurement technology
G3-01	Amagata	Nobuhiko	IIS	Simple and low-cost cell trap microfluidic device for detection of Malaria
G3-02	Favard	Alexandre	CNRS	Selectivity of integrated multi-sensor for BTEX detection
G3-03	Maaroufi	Seiffedine	CNRS	Reliability study of Piezoelectric Structures Dedicated to Energy Harvesting by the Way of Blocking Force Investigation
G3-04	Prater	Karin	EPFL	Glassy Carbon Masters for Plastic Injection Mdding
G3-05	Abboud	Zeinab	EPM	in situ investigations of gas trapping in getter material
G3-06	Doi	Kotaro	IIS	Reproducing podocyte's phenotype in vivo with filtration mechanostres
G3-07	Shi	Shuai	IIS	Research on super-lubricity and energy dissipation in micro/nano scale by using AFM
G3-08	Koduri Veera Venkata	Naga Rama Mani Mano- har Prasad	NTHU	Nano oxygen particles for oxygen sensing in cell culture
G3-09	Lee	Giyoon	SNU	Rapid antibiotic suceptibility test using single cell colony imaging
G3-10	Heikkinen	Marika	VTT	Array-based serotyping for autoimmune diseases and allergy

Poster List

Group Number	Last name	First name	Affiliation	Poster title
G4-01	Osawa	Hiroyasu	IIS	Colour atomic force microscopy - Towards AFM with chemical contrast
G4-02	Malbec	Rémi	CNRS	Lab on a chip for sample preparation and detection of circulating biomarkers in blood plasma
G4-03	Maqueda Lopez	Mariazel	EPFL	RF MEMS Resonators
G4-04	Banerjee	Kaustubh	IMTEK	Optofluidic Adaptive Optics
G4-05	Danoy	Mathieu	IIS	A novel hierarchical in-vitro coculture model of the liver microvascula- ture for pancreatic cancer cells adhesion monitoring
G4-06	George	Anthony	IIS	Low-Cost and Large Area Nanopatterning by Block
G4-07	Chicot	Edwing	IIS	Chemical contrast of nanostructured samples with atomic force mi- croscopy
G4-08	Keeler	Ethan	U. Wash- ington	Optical-Trapping Enhanced MEMS-Resonant Mass Detection for Biological Applications
G4-09	Cho	SeongKyu	SNU	Scalable Solar Cell with Micro Fluidic Self-Assembly
G4-10	McCaffrey	Colm	VTT	
G5-01	Baik	Gunwoong	IIS	Microfluidic device for the quantitative analysis of microvasculature network
G5-02	Wei	Jie	CNRS	Magnetic-less energy harvesting circuits for active mdeical implants
G5-03	Peric	Olivier	EPFL	Microfluidic Bacterial Traps for Simultaneous Fluorescence and Atomic Force Microscopy
G5-04	Chagnon	Dany	EPM	in situ Monitoring of Microstructure and Phase Changes of AuSn Solders for Hermetic Wafer-Level Packaging
G5-05	Shaik	Faruk Azam	IIS	Lab-On-a-Chip for bioassay applications
G5-06	Tachikawa	Saeko	IIS	Rea-time TEM observation of nano-contact for revealing the mecha- nisms of solid lubrication
G5-07	Pan	Zhenhai	IIS	Study on local surface properties of CIGS by EFM
G5-08	Han	Zheyi	U. Wash- ington	Etch Selectivity Improvement of Hydrogen Silsesquioxqne with Rapid Thermal Annealing
G5-09	Lee	Hyekyung	SNU	Concentration Independent Micro/nanofluidic Diode using Microscale Asymmetry of Ion Concentration Polarization Layer Induced by Leak- age Flow
G5-10	Elferink	William	MESA+	(no poster presentation:internship st)
G6-01	Sano	Chikako	IIS	Vibration energy harvester with ionic liquid based gel electret
G6-02	Donero	Laetitia	CNRS	Study of bottom gate field effect transistor for sensing application
G6-03	Milon	Nicolas	CNRS	Separation and isolation of large DNA fragments in viscoelastic solu- tion
G6-04	Ghadimi	Amir Hos- sein	EPFL	Ultra-high sensitive optomechanical sensor
G6-05	Kretschmer	Simon	IMTEK	MEMS endomicroscope for simultaneous white-light microscopy and Optical Coherence Tomography
G6-06	Wasser	Pierre	IIS	Embedded real time acquisition device for chemical contrast imaging on Atomic Force Microscopy
G6-07	Lee	Seung-ryeul	SNU	Engineering aligned 3D neural circuit in microfluidic device
G6-08	Gwon	Oh-Jun	SNU	Fabrication of a tactile sensor using a piezoresistive characteristic of reduced graphene oxide
G6-09	Jylhä	Sirpa	VTT	Potential of recombinant antibody fragments in microsystems
G6-10	Muttikulan- gara Swam- inathan	Sanathanan	NYU	Tunable Diffraction Grating for Imaging Spectrometer

Experiment by Nobel Prize laureate, Dr. Hideki Shirakawa



Hideki Shirakawa - Biographical

For the ten years from the third grade of elementary school to the end of high school, I lived in the small city of Takayama, a town of less than sixty thousand, located in the middle of Honshu, Japan. Even though it was far away from Japan's principal cities, Takayama has been called a "little Kyoto" because of the similarity of its landform to Kyoto, the city sits in a basin surrounded by mountains with a river flowing through it, and because of its long-established cultural heritage and tradition. In this small town, rich in natural beauty, I spent my days enthusiastically collecting insects and plants, and making radios. My affinity for science was awakened and grew during in these ten years.

Long after I became a polymer scientist, I occasionally remembered a short composition I had written during my last year in junior high school. At that time students compiled a commemorative collection of compositions describing our future dreams. As I recalled, I wrote something about my wish to be a scientist in the future and to conduct research on plastics useful for ordinary people. I cannot be sure what I wrote exactly because I lost the book of essays during repeated moves afterwards. I had long regretted this loss because I wanted to know more about why and how a junior high school boy decided on a future research career in plastics.

Much to my surprise, I found that the full composition I had lost was printed in every Japanese newspaper the day after the Royal Swedish Academy of

Sciences announced its award of the Nobel Prize in Chemistry for 2000 to two friends and myself. After 45 years, I could finally read the complete composition again. I was deeply impressed with the great power of the Nobel Prize.

I was born in Tokyo in August 1936, the third child of Hatsutarou, a medical doctor, and Fuyuno, a daughter of a chief priest of a Buddhist temple. After me, a sister and a brother were born, joining my elder brother, my elder sister and me. After I was born, my family moved many times, following my father's work, but we finally settled in Takayama, my mother's hometown, in 1944 during the confusion toward the end of the war.

My higher education began when I entered Tokyo Institute of Technology in April 1957. In March 1966, I completed my doctoral course and received the degree of Doctor of Engineering. In the same year, I married Chiyoko Shibuya, and we were later blessed with two sons, Chihiro and Yasuki.

There were three specific fields I wished to study at university. One was polymer chemistry, just as I had written in my junior high school composition. The other possibilities were horticulture and electronics. I had decided to major in polymer chemistry only if I successfully passed the entrance examination for Tokyo Institute of Technology. In April 1957, after entering Tokyo Institute of Technology, I mainly studied applied chemistry during my undergraduate career. In Japanese universities, an undergraduate major in an science course has to belong to one of the laboratories in his department during his final year in order to work on a graduation thesis. I was interested in synthesizing new polymers, so I applied to a laboratory conducting synthesis research. But since there were too many applicants who wanted to enter into the laboratory I had chosen, I had to switch to a laboratory working on polymer physics. Initially I was reluctant to work in this field, but actually, I realize that my experiences in this laboratory were of great importance to me when I worked with polyacetylene later on.

I finally began working on polymer synthesis, my original interest, in my graduate program, but I started the work on polyacetylene, the work for which I now share the Nobel Prize, just after I received my doctorate and I became a research associate in April 1966. The initial purpose of this study was to determine the polymierization mechanism of polyacetylene using the Ziegler-Natta catalysts. In the fall of 1967, only a short time after we started polyacetylene film through an unforeseeable experimental failure.

With the conventional method of polymerization, chemists had obtained polyacetylene in the form of black powder; however, one day, when a visiting scientist tried to make polyacetylene in the usual way, he only produced some ragged pieces of a film. In order to clarify the reason for the failure, I inspected various polymerization conditions again and again. I finally found that the concentration of the catalyst was the decisive factor for making the film. In any chemical reaction, a very small quantity of the catalyst, about mmol would be sufficient, but the result I got was for a quantity of mol, a thousand times higher than I had intended. It was an extraordinary unit for a catalyst. I might have missed the "m" for "mmol" in my experimental instructions, or the visitor might have misread it. For whatever reason, he had added the catalyst of some molar quantities in the reaction vessel. The catalyst concentration of a thousand-fold higher than I had planned apparently accelerated the rate of the polymerization reaction about a thousand times. Roughly speaking, as soon as acetylene gas was put into the catalyst, the reaction occurred so quickly that the gas was just polymerized on the surface of the catalyst as a thin film.

But we noticed another important factor besides the concentration of the catalyst. Polyacetylene has a property of being insoluble in any solvent, a property which contributed to the formation of the film. Even more surprising, when we observed the film through a transmission electron microscope, we saw that the film was composed of long entangled micro-fibers of polyacetylene. These two properties are essential for the formation of any film, and they were inherent in polyacetylene.

One more important factor contributed to the formation of the film was the Ziegler-Natta catalyst we had used. Most of the Ziegler-Natta catalysts tend to form precipitates which give an inhomogeneous solution. From such an inhomogeneous catalyst, it is very difficult to form polyacetylene film. But the Ziegler-Natta catalyst we had used in our experiment was a unique one. It had good solubility in organic solvents to give a homogeneous solution and it also had high activity to give a high molecular weight and crystalline form of polyacetylene. I could say that nature had prepared us for the way to make polyacetylene film. Later, through the measurements of various absorption spectra of this thin film, we determined the molecular structure of polyacetylene, and thus, we fulfilled the initial purpose of our work.

By chance, this glittering, silvery film, caught the eyes of Professor Alan G. MacDiarmid, one of the co-recipients of the prize, and he invited me to work with him in the U.S.A. In September 1976, I went to the University of Pennsylvania, where Professor Alan J. Heeger, another co-recipient, was also working, and I spent one year there.

I still vividly remember the day of November 23, 1976. With Dr. C.K. Chiang, a postdoctoral fellow who was working under Professor Heeger, I was measuring the electric conductivity of polyacetylene by the four-probe method, adding bromine. At exactly the moment we added bromine, the conductivity jumped so rapidly that he couldn't switch the range of the electrometers. Actually, the conductivity was ten million times higher than before adding bromine. This day marked the first time we observed the doping effect, although it was a pity that the expensive equipment was broken. The discovery of chemical doping is one of the representative results of our collaboration in this period.

After returning to Japan, I continued to work on polyacetylene. What I did first was to shed light on the chemical reaction associated with the doping phenomena. In cooperation with many co-workers, I investigated various spectra of the doped polyacetylene films: infrared absorption, Raman scattering, ultraviolet-visible absorption, the Mössbauer effect, and EXAFS. As a result, we found that the emergence of electrical conductivity on the doped polyacetylene was due to the creation of carbocations or positively charged solitons associated with withdrawing of p electrons from polyacetylene by the dopant when iodine was used as an acceptor dopant.

In November 1979, I moved from Tokyo Institute of Technology to the Institute of Materials Science, University of Tsukuba, where I was appointed Associate Professor. In October 1982, I was promoted to full professor and worked on polyacetylene and other conducting polymers. Since my retirement from University of Tsukuba at the end of March 2000, I have withdrawn from scientific research and other educational activities.

Let me mention two of my major contributions to polyacetylene research during my time at Tsukuba. One is the preparation of oriented films. The significance of polyacetylene being a typical quasi-one dimensional material was recognized very early. In this sense, an oriented film was indispensable to study the intrinsic one-dimensional properties. The polyacetylene films synthesized until then were an isotropic material in which the fibrils were entangled in three-dimensional disorder. I came up with the idea to directly synthesize the uniaxially oriented films by using liquid crystal as a solvent. The same idea was proposed by a scientist from a company. We found that an equimolar mixture of nematic liquid crystals bearing a phenylcyclohexyl moiety was useful for that purpose. We succeeded in simultaneously polymerizing acetylene and synthesizing uniaxially oriented polyacetylene films by orienting the catalyst solution of liquid crystal solvent under flow condition or magnetic field. Further development of this technique enabled us to synthesize helical polyacetylene that consists of clockwise or counterclockwise helical structure of fibrils, by use of chiral nematic liquid crystals. The chiral helicity of the films may be useful for electromagnetic and optical applications.

The other contribution is the synthesis of liquid crystalline conjugated polymers by replacing the hydrogen atom bonded to polyacetylene with a substituent having liquid crystalline nature as the side chain. As these polymers have large substituents, the doping effect is poor. However, these polymers can be modified by introducing various substituents with interesting optical and thermal properties. In addition, they can orient spontaneously in a given range of temperature.

Some other details to be mentioned

Chair of Master's School in Sciences and Engineering, Graduate School, University of Tsukuba, April 1991-March 1993. Provost of the 3rd Cluster of Colleges, University of Tsukuba, April 1994-March 1997.

Honors

The Award of the Society of Polymer Science, Japan (1982), May 1983.

Award for Distinguished Service in Advancement of Polymer Science, the Society of Polymer Science, Japan (1999), May 2000.

Person of Cultural Merits, November 2000. Order of Culture, November 2000.

This autobiography/biography was written at the time of the award and later published in the book series Les Prix Nobel/ Nobel Lectures/The Nobel Prizes. The information is sometimes updated with an addendum submitted by the Laureate.

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http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2000/shirakawa-bio.html

FUNDAMENTALS OF CONDUCTIVE POLYMERS

Hideki Shirakawa

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History of Conductive Polymer Development

Serendipity

Straight-chain compounds, which consist of alternately linked single bonds and double bonds [-(CH=CH)_n-], are called conjugated polyenes; physicists as well as chemists have long been interested in them. From early on, synthetic organic chemists knew a phenomenon in which with increases in the conjugate number (n), the maximum of the absorption spectrum shifts to longer wavelength region (bathochromic effect), and simultaneously, the absorbance increases (hyperchromic effect). In linear polyenes with larger conjugate numbers, single bonds get shorter while double bonds are longer. It is expected that a bond is intermediate between single and double bonds for an infinitely long conjugated polyene where the lengths of single and double bonds tend to be equal. In this state, an infinite number of π (pi) orbitals form continuous energy states (i.e., energy bands). The bonding orbitals, consisting of an infinite number of π electrons occupy the lower half of the bands (valence band) adjacent to the upper half of the empty band (conduction band), which is a characteristic band structure corresponding to metals. Accordingly, some of the π electrons are excited from the valence band to the conduction band even at normal temperature (energy corresponding to normal temperature), thus exhibiting electrical conductivity. This is why infinitely long conjugated polyenes became a popular topic of scientific conversation as a metal model or a free electron model. Later, however, it was theoretically demonstrated that the molecular structure allowing the bond alternation is more energetically stable by taking σ (sigma) electrons as well as π electrons into consideration, negating the metallic model.

Solid-state physicists tend to explain the total energy of a molecule as the sum of electron energy and lattice energy. For example, the lattice of a conjugated polyene is regarded as a property associated with the positions of the carbon atoms that form its linear chain, and when the lattice spacing (the length of a carbon-carbon bond) is uniform, lattice energy will be at a minimum. On the other hand, since electrons have a strong tendency to form pairs of opposite-spin electrons, chemical bonds with diverse bond lengths allow lower electron energy. In other words, lattice energy and electron energy have conflicting characteristics. In particular, a linear molecule consisting of a one-dimensional arrangement of carbon-carbon bonds, such as a conjugated polyene, has markedly weak binding force in the other two dimensional directions. Accordingly, a decrease in electron energy determines the total energy of the molecule by contributing to offsetting the disadvantage of an energy increase that causes lattice deformation (which induces bond alternation). Bond alternation causes a gap (Δ Eg) between the valence band and the conduction band, and the magnitude of the gap varies depending on the degree of the bond alternation. When the gap is small (≤1.5 eV), the

molecule becomes a semiconductor; when the gap is large (>1.5 eV), the molecule becomes an insulator.

Conjugated polyenes with larger conjugate numbers exhibit remarkably poor solubility to any solvent. Accordingly, it was extremely difficult to synthesize molecules corresponding to infinitely long conjugated polyenes to demonstrate their bond alternative characteristics. Finally, in 1958, G. Natta et al. reported the synthesis of a polymer³ corresponding to an infinitely long conjugated polyene by a catalytic polymerization of acetylene using the Ziegler-Natta catalyst, which is a well-known catalyst for polymerization of polyethylene and polypropylene.

In the latter half of the 1960s, Shirakawa, one of the winners of the 2000 Nobel Prize in Chemistry with A. J. Heeger and A. MacDiarmid was studying the polymerization reaction of acetylene with the aid of the Ziegler-Natta catalyst at the Tokyo Institute of Technology. Initially, he did not intend to create conductive polymers, but mainly intended to investigate the mechanism of polyacetylene polymerization reaction.⁴ Researchers in those days could only produce a black powder of polyacetylene no matter what they tried. The substance was insoluble in any solvent and unmeltable at high temperatures. Neither heating nor dissolving in solvent softened the polymer. It could not be formed into arbitrary shapes and generally lacked the merits of a plastic, to the extent that one would be hard-pressed to find a use for it.⁵

Around 1967, however, a polyacetylene thin film, which nobody had been able to create, was synthesized almost by chance when a visiting scientist who had joined the Ikeda group of the Tokyo Institute of Technology expressed his wish to try synthesizing polyacetylene. Shirakawa, who was then a member of the group, taught the visiting scientist a normal catalytic recipe and allowed him to perform an experiment. After a while, the visiting scientist reported to him that the experiment had failed. What Shirakawa saw when he went to examine the result of the reaction was a black film on the surface of the catalyst solution. A black film had been formed instead of polyacetylene powder. Moreover, the pressure gauge indicated almost no acetylene had been polymerized. The experiment had not achieved its original purpose, so it had clearly "failed."

Shirakawa did not want to repeat the same failure, so he performed a detailed analysis of the black film. Then, things changed drastically. The black film was without a doubt a polyacetylene film. Shirakawa started experiments to intentionally create a polyacetylene film. In the course of investigating polyacetylene formation conditions, he found that polyacetylene film tends to form in a catalytic solution more concentrated than the conventional solution. Specifically, he hypothesized that the wrong units had been used to measure the concentration of the catalytic solution. The visiting scientist might have mistakenly measured the concentration using mols instead the mmols called for in the recipe. That is 1,000 times stronger than the original recipe! The amazing part of this discovery is that the visiting scientist mistakenly did what common-sense chemists would never have thought of doing. Then Shirakawa saw the value of the experiment, which otherwise might have been regarded as a mere failure. That is why this incident is regarded as an example of serendipity.

Thus, polyacetylene films were successfully synthesized, and experiments associated with its synthesis were repeated. In the course of the study, they observed that polyacetylene films show a metallic sheen. Seeing the sheen, Shirakawa thought that the film might conduct electricity. This is the second moment of serendipity in this discovery. Certainly, the Kambara and Hatano group of the Tokyo Institute of Technology had originally been studying polyacetylene powder and discovered that it is a polymeric organic semiconductor. However, the inspiration that electrically insulating polymers might conduct electricity under a special condition plowed the way to the discovery of doped polyacetylene as the world's first electrically conductive polymer.

Although polyacetylene in the form of a film had been discovered, the journey was far from over. The measured electrical resistivity and band gap of undoped polyacetylene films were exactly in the ranges of those for semiconductors or insulators.

 1.0×10^4 ohm·cm and 0.56 eV for *trans* form of polyacetylene;

 2.4×10^8 ohm cm and 0.93 eV for *cis* form of polyacetylene.

In addition, for better or for worse, no researchers were interested in the reported research achievements and no competing researchers appeared.⁶

However, another wonderful opportunity came to Shirakawa. An inorganic chemist, MacDiarmid of the University of Pennsylvania, became interested in polyacetylene, this humble organic polymer that possesses a metallic sheen. In 1976, Shirakawa was invited to the University of Pennsylvania and started research in cooperation with MacDiarmid and Heeger, a solid-state physicist. As part of their research, they proposed chemical doping, which creates holes to move along the polymer main chain, by adding a trace amount of electrophilic halogen atoms (initially, bromine molecules were used, and later, iodine). Chemical doping brought about a surprising result. The electrical conductivity of polyacetylene jumped to a level 10 million times higher than that of conventional polyacetylene, and subsequent study achieved electrical conductivities of several thousand S/cms, which is comparable to those of typical metals. Thus, the conductive polymer polyacetylene was born.

Polyacetylene, the first conductive polymer had a great impact on the scientific world and drew attention as one of the greatest discoveries in the world. Shirakawa called it "modern-day alchemy,"⁶ and it is no exaggeration to call it that. After its creation, various studies were conducted on the synthesis and application of polyacetylene. A research team at BASF reported that they synthesized polyacetylene with electrical conductivity on the order of 10⁵ S/cm by using silicon oil as a solvent and aging the catalyst solution at high temperature. However, to our knowledge, no one else has reported success in obtaining the same result. In addition, studies on the expected applications of polyacetylene seem to have encountered difficulty caused by its low environmental stability at ambient conditions. Given this situation, it is interesting to note that more than 30 years ago, researchers were conducting studies that seem to have predicted the present circumstances regarding batteries. Shirakawa et al. made prototypes of organic thin film solar cells based on polyacetylene and Akira Yoshino of Asahi Kasei Corporation, who is now known as the inventor of the lithium-ion battery, was researching polyacetylene as a material for electrodes in batteries.

Characteristics of Conductive Polymers

Conductive polymers such as polyacetylene are synthesized with electrical properties ranging from insulators to semiconductors. They are converted from semiconductors to conductors (becoming electrically conductive polymers) by a doping process, which will be described later. Then, what makes electrically conductive polymers represented by polyacetylene differ from general-purpose polymers such as polyethylene? The answer is the difference in their molecular structure.

Polyethylene (Figure 1) and polyacetylene (Figure 2) seem to have a similar structure. However, the main chain of polyethylene molecule consists only of single bonds, strong σ bonds, whereas that of polyacetylene has a conjugated structure, in which alternate single and double bonds (σ and π bonds, respectively) repeatedly continue. This conjugated structure is a decisive factor in its electrical conductivity.



Figure 1. Molecular Structure of Polyethylene



Figure 2. Molecular Structure of Polyacetylene (Trans Form

As shown in **Figure 3**, every carbon atom forming the main chain of polyacetylene (*trans* form) has a *p* orbital (also called a π orbital) occupied by a π electron. In other words, π electrons are considered to be arranged in one dimension. However, since each π electron simultaneously belongs to two adjacent π orbitals to contribute to the formation of a double bond, it cannot move freely resulting in the π electron localization. Therefore polyacetylene is an insulator or, at best, a semiconductor.



Figure 3. p Orbitals and π Electrons in Polyacetylene

Imparting electrical conductivity to the polymer requires a process (or reaction) called doping, specifically chemical doping. The actual process of doping is an addition of a small amount of a reagent shown in **Table 1** (including acceptors which tend to readily accept electrons and donors which tend to readily donate electrons). Chemical doping induces electrical conductivity in the polymers.

Table 1. Types of Dopants

Dopant Types	
Acceptor	
Halogen	Br ₂ , I ₂ , ICI, ICI ₃
Lewis acid	PF ₅ , AsF ₅ , BF ₃ , SO ₃
Proton acid	HCI, H ₂ SO ₄ , HCIO ₄
Transition metal halide	FeCl ₃ , FeBr ₃ , SnCl ₄
Organic compound	TCNE, TCNQ, DDQ, Various amino acids
Electrochemical doping	CIO ₄ ', BF ₄ ', PF ₆ ', AsF ₆ '
Donor	
Alkaline metal	Li, Na, K, Rb, Cs
Alkaline earth metal	Be, Mg, Ca
Electrochemical doping	Li ⁺ , Na ⁺ , K ⁺ , R ₄ N ⁺ , R ₄ P ⁺ (R=CH ₃ , C ₆ H ₅ , etc.)

Doping can also be carried out in an electrochemical manner by applying a voltage between a positive and negative electrode made of conductive polymer in an electrolytic solution containing an electrolyte (D+A). Acceptor doping occurs at the positive electrode, and donor doping occurs at the negative electrode.

An addition of acceptor or donor induces electrical conductivity of the conjugated polymers. The acceptor extracts π electrons from the conjugated polymer to form positive charge carriers (holes) and the donor supplies electrons to the conjugated polymer to form negative charge carriers.

The *trans* form of polyacetylene may have two isomeric structures with an ascending double bond (here called phase A) and with a descending double bond (here called phase B). The two conjugated structures are symmetric with each other and cannot be distinguished in energy. This system is termed a degenerated state. Among the different kinds of conjugated polymers, only the *trans* form of polyacetylene has this structure.

ESR measurement has revealed that the trans form of polyacetylene has 3×10^{19} spin/g of unpaired electrons. On the other hand, no unpaired electrons are observed in the carefully synthesized cis form of polyacetylene, and a cis form of polyacetylene synthesized at low temperature irreversibly turns into the *trans* form of polyacetylene by thermal isomerization. Accordingly, it is considered that an isolated π electron forms between phase A and B by a rearrangement of the conjugation during the thermal isomerization. In other words, a stabilized state where an isolated unpaired π electron exists in the boundary of the two phases is induced. The isolated π electron is called a neutral soliton. Since the isolated π electrons have no electric charge, they do not act as charge carriers. However, they exhibit higher reactivity than paired π electrons so that they tend to react with acceptors to form negatively charged solitons or with donors to form positively charged solitons, contributing to inducing electrical conductivity in polyacetylene (Figure 4).



Figure 4. Unpaired Electrons (Neutral Solitons) Created in *Trans* Form of Polyacetylene with Degenerated Structure

Conjugated polymers other than the *trans* form of polyacetylene are nondegenerate systems, in which extraction or rearrangement of π electrons produces two structures with different energy states. For example, in a poly (*p*-phenylene), when an acceptor dopant extracts π electrons from its double bonds, the bonds are rearranged to convert from a stable benzenoid structure (phase A) into a quinoid structure (phase B), a higher-energy state. Since the conversion into phase B requires energy equivalent to the energy difference between two states, limited domains are turned into phase B to create polarons (**Figure 5**).



Figure 5. Positive Polarons Created in Poly (p-phenylene) with Nondegenerate Structure

In the acceptor doping process, the acceptor extracts isolated π electrons from a polaron to form a positively charged bipolaron that has two positive charges, and the donor doping supplies an electron to form a negatively charged bipolaron having two negative charges (Table 2 and Figure 6).

The doping process not only converts the electrical conductivity from an insulator level to a conductor level, it also brings about various physical property changes such as color and size in the conductive polymers. Thus, the doping process is what makes the diversity of applications of the conductive polymers possible.

Table 2. Types of Charge Carriers in Conductive Polymers

Electric Charge	Number of Charges	Spin
Soliton Charge Carriers		
Neutral	0	1/2
Positive	+1	0
Negative	-1	0
Polaron Charge Carriers		
Positive	+1	1/2
Negative	-1	1/2
Bipolaron Charge Carriers		
Positive	+2	0
Negative	-2	0



Figure 6. Energy Level Diagram of Charge Carriers

As seen in **Figure 7**, for example, when iodine is added to polyacetylene as a dopant, iodine removes π electrons in the polymer main chain and leaves holes there. To explain this in more visual terms, polyactyelene before doping can be considered as a crowded train in which passengers are so packed they cannot move. Passengers in the train are equivalent to the electrons in polyacetylene. If some passengers get off (i.e., π electrons are removed by a dopant), space is created for nearby passengers to move into first. The newly vacated space is then available for the remaining passengers to move into. As a result, passengers can move as a whole. Electrons also move in this manner. When a voltage is applied to the polyacetylene, holes and electrons move successively; thus, electric current flows (**Figure 8**).



Figure 7. Chemical Doping in Polyacetylene



Figure 8. Electric Conduction in Polyacetylene

Evolution of Conductive Polymers

While the potential of polyacetylene has been highly regarded, conductive polymers containing aromatic rings have been developed one after another. Since they have superior air stability, they have been put into practical use. Polyacetylene, a typical aliphatic conjugated compound, tends to induce the electrophilic addition reaction in its double bonds. As a result of the addition reaction, the conjugated system of polyacetylene is cut off, so that its doping susceptibility is easily lost. On the other hand, aromatic conjugated compounds do not have the tendency to induce the addition reaction in their double bonds and are, therefore, more chemically stable than their aliphatic conjugated counterpart. Figure 9 shows structures of conductive polymers containing aromatic rings. Table 3 summarizes the classification of conductive polymers.



Figure 9. Conductive Polymers Containing Aromatic Rings

Table 3. Classification of Conductive Polymers

Types of Carriers	
Conjugated-system Polymers	Representative Polymer
Aliphatic conjugated system	Polyacetylene
Aromatic conjugated system	Poly(p-phenylene)
Mixed-type conjugated system	Poly(p-phenylene vinylene)
Heterocyclic conjugated system	Polypyrrole, polythiophene, PEDOT
Heteroatomic conjugated system	Polyaniline
Double-stranded conjugated system	Polyacene (virtual molecule)
Two-dimensional conjugated system	Graphene

In terms of application, polypyrrole (Aldrich Prod. Nos. 482552, 577030, 578177, 530573, and 577065) is probably the most common. However, very few people know in what everyday products they encounter polypyrrole. Polypyrrole that has undergone doping with an acceptor is stable (Aldrich Prod. No. 482552, etc.). It can be easily synthesized from pyrrole (Aldrich Prod. No. 131709) by oxidation polymerization. One of its applications is the solid electrolytic capacitor. Generally, the electrolyte solution in electrolytic capacitors is an ion conductor, so its electric conductivity is low, resulting in its bad frequency characteristics (the impedance increases in the high-frequency region).⁷ Use of doped polypyrrole instead of electrolyte solution drastically improves the frequency characteristics and allows small, light-weight, and high-capacity polymer solid electrolytic capacitors to be produced. The polypyrrolebased solid electrolytic capacitors (as backup capacitors used when a power supply suddenly goes off) are superior in noise removal, ripple absorption, and the decoupling effect. Therefore, these capacitors have already been used in many applications, such as cellular phones, notebook computers, handheld games, and portable audio players, and have greatly contributed to the creation of the small, light-weight, and high-performance products that we are using in our everyday lives.

Polyaniline is also easily synthesized from its inexpensive raw material, aniline, by oxidation polymerization. Since the early stage of research on conductive polymers, it has been well studied as the most promising material for practical use. Polyaniline takes four different states depending on the type of treatment applied after its synthesis. However, the only electrically conductive polyaniline is the dark-green emeraldine salt. Heeger et al. used a functional dopant, such as camphorsulfonic acid (CSA) and dodecylbenzenesulfonic acid (DBSA, Aldrich Prod. No. 522953) to create polyaniline that is soluble in cresol and xylene while maintaining its electric conductivity. Around the same time, various applications for polyaniline were created in parallel, and research on devices with polyaniline electrodes (i.e., a transistor, a polymeric lithium battery, and a dye-sensitized solar cell) was reported one after another.⁸ Polyaniline is also used in products more familiar to us, such as antistatic films and neutralization units in copiers. Various types of polyaniline products are commercially available. They can also be purchased from Sigma-Aldrich (Aldrich Prod. Nos. 428329, 476706, 530565, 530689, 556378, 556386, 556459, etc.)

In the 1990s, R. H. Friend et al. of Cambridge University reported on the electroluminescence (EL) of a conductive polymer, polyphenylenevinylene.⁹ This report inspired other researchers to research polymeric organic EL materials using conductive polymers. Their research was based on the semiconducting characteristics of undoped conductive polymers, and the term "conjugated polymers" also came into common use. Conductive polymers emit different luminescent colors depending on the design of their molecular structure, that is, the degree of their conjugation length. For example, polyphenylene and polyfluorene emit blue to aqua light, polyphenylene vinylene emits green to orange light, and polythienylenevinylene emits orange to red light. It is possible to produce the three primary colors using only conductive polymers. The details of polymeric organic EL materials, such as device structure, are described in Material Matters™ Basics Vol. 1: The Fundamentals and Fabrication Technology of Organic EL Devices¹⁰ and Material Matters™ Vol. 2, No. 3: Organic Electronics.11 Today, organic EL displays using low molecular weight organic EL materials are coming into increasingly wide use. However, it seems that polymeric organic EL materials based mainly on easily processable conductive polymers may be substituted for them sooner or later.

The top runner of the latest conductive polymers is poly(3,4-ethylene dioxythiophene) (PEDOT). Research on PEDOT has been conducted worldwide, and some technical books specializing in PEDOT have been published.^{12,13} In a sense, PEDOT, which possesses excellent stability, high electrical conductivity, high hole injection capacity, and flexible doping characteristics, is an ideal conductive polymer. PEDOT/PSS (Aldrich Prod. Nos. 768642, 739340, 739332, 739324, 739316, 655201, 483095, and 560596) is a commercially available water or organic-solvent solution in which polystyrenesulfonic acid (PSS) is dispersed in the form of a polymer dopant. It allows conductive polymer films with any desired thickness to be easily produced by spin coating and thereby has carved a new way for organic electronics. In this field, a technology for equalizing the particle sizes of PEDOT to form uniform films has been established.

As described in the above application examples of conductive polymers, PEDOT is finding applications in increasingly wide areas, such as capacitors, transistors, antistatic films, and batteries. In addition, applied research on PEDOT is being performed in incomparable diverse fields¹² associated with devices, such as actuators, sensors, and thermoelectric transducers. For example, in the field of actuators, artificial muscle that is not only strong and flexible, but also electrically conductive is under development by combining mechanically tough double network hydrogel and PEDOT. Thus, so-called hybridization with other functional materials is advancing, which in turn inspires research in this field.

Of particular note is PEDOT's superior hole injection capacity, making it commonly used as a material for the hole injection and transport layer of organic EL devices. In addition, PEDOT/PSS is widely used as a material for the hole transport layer of organic thin film solar cells. The details of their device structure are described in *Material Matters*[™] *Basics Vol. 4: The Fundamentals of Organic Thin Film Solar Cells.*¹⁴ A close look at the device structure reveals that blends of a poly (3-alkylthiophene: P3HT (Aldrich Prod. Nos. 445703, 698989, and 698997)) in the polythiophene family and a modified fullerene (phenyl-C61-butyrate methyl ester: PCBM (Aldrich Prod. Nos. 684430, 684449, and 684457)) have been widely adopted as materials for the photoelectric conversion layer of organic thin film solar cells. In addition, polythiophene has been regarded as a promising material for organic transistors, and research on it has long been conducted. The details are described in *Material Matters™ Basics Vol. 6: The Fundamentals of Organic Transistors.*¹⁵

Moreover, PEDOT/PSS, which exhibits low visible light absorption, is expected to be a material able to substitute for indium-tin oxide (ITO), which is absolutely necessary as a transparent electrode material. PEDOT/ PSS makes it possible to eliminate the use of toxic lead and the rare metal, indium. Since it is a polymer material, it is also excellent in flexibility and elasticity. It can be used in products for our everyday lives, such as touch panels, and is expected to be used in displays of the future that were once considered to be science fiction, such as flexible electronic paper.

Although it is an excellent material, there also remain issues to be solved regarding PEDOT/PSS. For example, when PSS is used as its dopant, it inevitably develops a light absorption characteristic in the visible light region. It has been reported¹⁶ that substituting polyvinylsulfonic acid (PVS) with no benzene ring for PSS as its dopant suppresses light absorption in the visible light region. In addition, the performance and service life of organic EL devices have been enhanced by lamination. It has been pointed out¹⁷ that the use of PEDOT/PSS for the hole injection layer of organic EL devices may cause the devices to degrade faster than normal because of sulfonic acid, a strong acid. Therefore, dopants for PEDOT and substitute hole transport materials for PEDOT/PSS are under study.¹⁸

The processing methods of conductive polymers, such as jet printing, spray film formation, and Roll-to-Roll, are essential for application of conductive polymers including PEDOT/PSS to devices, such as organic EL devices, organic solar cells, and electrode materials. These processing methods may serve to create lower-price, higher-performance conductive polymer devices, so various types of research and development on the methods are actively being performed. Particularly, in jet printing technology, some printing devices that can spray PEDOT nanoparticles have been developed and allow nanolevel writing and patterning. This technology will make it unnecessary to rely on large-scale devices, such as deposition apparatuses and photolithography equipment, and will realize printable electronics, bottom-up technology that makes it possible to arrange "necessary quantities" of "necessary materials" in "necessary locations." Simultaneous advancement of printable electronics and conductive polymer technology is sure to bring about a major breakthrough not only in the field of organic electronics, but also in the entire field of electronic devices.

Thus far we have outlined conductive polymers and their applications. Now we move on to another value of conductive polymers—their application in scientific education.

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