Events

MANA Second-term Kickoff Meeting was Held

Auditorium in the new WPI-MANA Building.

On May 7, 2012, MANA Director-General Masakazu Aono gave a talk to all MANA staff in the Auditorium of the new WPI-MANA Building. He presented the history of MANA over the past 5 years. Then he emphasized the importance of promoting research in the four research fields of MANA based on the concept of “materials nanoarchitectonics” and explained the outline of MANA’s activities for the next 5 years. After the meeting, a Kickoff party was held at the Melting Pot Café in the new building.

Australia / MANA Joint Workshop on Nanoarchitectonics for Innovative Materials & Systems

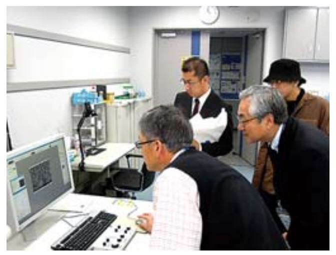
Prof. Tom Healy
(The University of Melbourne)

Prof. Neil Furlong
(The University of Melbourne)

On May 10, 2012, MANA and universities including the University of Melbourne from Australia jointly held a workshop entitled "Nanoarchitectonics for Innovative Materials & Systems". After the opening address by Prof. Neil Furlong from University of Melbourne and Dr. Kohei Uosaki, MANA Principal Investigator, 15 oral presentations were given by researchers from both institutes including invited researchers from a wide variety of fields including nanotechnology, materials science, medical science, environmental and energy. Active discussions on the latest research results were held by the 98 participants.

Open House 2012 at MANA

On April 18, MANA opened its facilities at Namiki Site to the general public as one of the research divisions of NIMS, acting with the 53rd Science and Technology Week from April 16 to 22 promoted by the Ministry of Education, Culture, Sports, Science & Technology in Japan. The Science and Technology Week is an event that aims to promote understanding of science and technology for the general public. Approximately 150 visitors enjoyed 10 scientific exhibitions and demonstrations by researchers at MANA.



Demonstration of Scanning Electron Microscope

Awards

Prof. Françoise Winnik Won the 2012 CIC Award

Prof. Françoise Winnik (Center)

On January 23, Chemical Institute of Canada (CIC) announced the winner of CIC Awards 2012 and Prof. Françoise Winnik, MANA Satellite Principal Investigator, won the 2012 Macromolecular Science and Engineering Award. This award is presented to an individual who, while residing in Canada, has made a distinguished contribution to macromolecular science or engineering. The award was given at the annual Canadian Chemistry Conference in Calgary on May 29, 2012.

Dr. Minoru Osada Awarded the 7th NIMS President’s Prize

Dr. Minoru Osada

Dr. Minoru Osada, MANA Associate Principal Investigator, received the 7th NIMS President's Research Encouragement Award on April 2, 2012. The award was given to him for his outstanding contribution to the field of Materials Science through his work on "Novel Physical Properties of Oxide Nanosheets and Their Applications".

Dr. Satoshi Tominaka Received the Funai Research Incentive Award

At the award ceremony:
Dr. Satoshi Tominaka (right)

Dr. Satoshi Tominaka, MANA Independent Scientist, received the Funai Research Incentive Award from Funai Foundation for Information Technology on April 14, 2012. The prize is awarded to researchers for excellent contributions to research in fields related to information technology and Information Science in Japan. The award was given to Dr. Tominaka for his marked work on "Creation of On-Chip Fuel Cells for Ultrasmall Electronics".

Newly Appointed Researchers

◆Associate Principal Investigator◆

Dr. Minoru Osada

◆MANA Scientist◆

Dr. Isao Ohkubo

Dr. Hiori Kino

◆Independent Scientist◆

Dr. Takeo Minari

Dr. Satoshi Tominaka

Dr. Daniele Pergolesi

Three new ICYS-MANA Researchers also joined MANA.

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“CONVERGENCE” is the keyword used to symbolically describe the entire project of MANA, where outstanding researchers from around the world assemble and converge in the “melting pot” research environment to bring together key technologies into nanoarchitechtonics for the creation and innovation of new functional materials.

wpi MANA
International Center for Materials Nanoarchitectonics (MANA)
No.11
Jun. 2012

CONVERGENCE

Systematic Exploration and New Concepts - The Catalyst for Innovative Research Initiatives

— Ei-ichi NEGISHI

Sustained Research in Japan Gains Recognition

— Dmitri GOLBERG

Construction of New Research Complex Complete —NanoGREEN / WPI-MANA Building

MANA’s Research Outcome

Highly Efficient Photoenergy Conversion Based on Surface Nanoarchitectonics — Kohei UOSAKI

Development of Thermoelectric Materials: Atomic Structure Level, Grain-size Level — Takao MORI

Smart Biomaterials to Control Stem Cell Differentiation - Designing Instructive Scaffolds for Cardiac Tissue Engineering - — Giancarlo FORTE

Charge-free Reverse Wormlike Micelles: Self-assembly beyond Conventional Common Sense — Lok Kumar SHRESTHA

Systematic Exploration and New Concepts - The Catalyst for Innovative Research Initiatives

✣ Interviewew: Akio ETORI, Science Journalist

Ei-ichi NEGISHI

After graduating from the Department of Applied Chemistry of the School of Engineering at the University of Tokyo in 1958, Dr. Negishi gained a job at Teijin Corporation, Tokyo. He then earned a Fulbright scholarship to study at the University of Pennsylvania, USA, in 1960 while still maintaining his employment status at Teijin Corporation. He subsequently obtained a PhD (Science) from the University of Pennsylvania in 1963. After leaving Teijin in 1966 he became a postdoctoral researcher under the mentorship of the Purdue chemistry professor Herbert C. Brown (1979 Nobel Laureate in Chemistry). Dr. Negishi was then promoted to becoming an assistant to Professor Brown in 1968, before moving to Syracuse University in 1972. In 1979 Dr. Negishi was invited to join the Purdue faculty as a professor, and was later promoted to the inaugural Herbert C. Brown Distinguished Professor of Chemistry in 1999. He was awarded the 2010 Nobel Chemistry Prize, alongside Richard Heck and Akira Suzuki, for his work on the 'Negishi coupling,' a precise palladium-catalyzed cross-coupling method using aluminum (1976), zinc (1977), zirconium (1977), and other organometallic derivatives. In addition to national awards and recognition that include the Chemical Society of Japan Award (1996), the Yamada-Koga Prize (2007), and the Order of Culture and Persons of Cultural Merit Award (2010), Dr. Negishi has also received a variety of international recognition which include the Harrison Fellowship at the University Pennsylvania (1962−1963), the A. R. Day Award (1996), the American Chemical Society Award in Organometallic Chemistry (1998), the Alexander von Humboldt Senior Researcher Award (1998−2001), the Herbert N. McCoy Award (1998), the Sir Edward Frankland Prize Lectureship (2001), and the American Chemical Society Award for Creative Works in Organic Synthesis (2010).

Enthusiasm for Organometallic Chemistry

—When did you first encounter cross-coupling?

Two years after joining Teijin I was given the chance to study at the University of Pennsylvania, USA, under a Fulbright scholarship for 3 years, starting in 1960. I had just turned 25 years old then. I did quite well in my first year of graduate studies, which provided me with confidence that I had the ability to be a researcher. Around that time I first started considering my future academic career.

I still recall a number of world leading scientists including both Nobel Prize winners and those who were to subsequently receive the Nobel Prize, visiting the University of Pennsylvania for presenting lectures. Purdue professor Herbert C Brown, my life-time mentor, visited Pennsylvania to lecture in 1962. He succeeded in synthesizing organoboron compounds in 1956, when modern organometallic chemistry was still a newly emerging scientific field. Much later he received the 1979 Nobel Prize in Chemistry for his work on developing the use of boron-containing compounds into important reagents for use in organic synthesis. In a 1962 presentation he made at the University of Pennsylvania he discussed his discovery of hydroboration, a hydrometallation reaction. After attending his presentation I felt certain that I had a definite interest in that type of work.

The 'Hits-Man' Style Goes a Long Way

—Did you then continue to work with Professor Brown?

No, I had to return to Japan for 3 years, as I was there on a Fulbright grant (1960-1963). So, I returned to Teijin to resume my research position. My assignments at the time were mostly unrelated to organometallic chemistry. Aside from that, I felt confident that the projects I pursued during the 1963-1966 period showed considerable success and industrial promise. However, commercial application of our research was not approved at a corporate meeting as it was considered not sufficiently attractive and the timing was premature. I was of course devastated when I learnt that managerial decision. I then realized that research excellence was insufficient within a corporate framework, and that I was not the person to make the final decision on the research I was involved in. The corporate managerial system is somewhat like baseball in that it does not matter how many hits you make unless you or your teammates actually get to the home plate.

Everybody must be familiar with the batting performance of the major league player Ichiro Suzuki. He has amassed a large number of single hits, second-base hits, and so on, and has been recognized as the 'Hits Man.' I wanted to be in control of my own life as an academic researcher, and make the final judgments on my own personal research, while accumulating results in a steady and consistent manner. At the same time, however, I could no longer contain my enthusiasm for research in organometallic chemistry.

Hoping to find a suitable research position in the USA, I then applied for a total of 10 postdoctoral job opportunities. I eventually received 3 offers including Professor Brown's. I worked with Professor Brown at Purdue for a total of 6 years beginning in 1966. I served as a postdoc for the first 2 years, and then as an assistant to Professor Brown for the remaining 4 years. Then I successfully gained an assistant professor position at Syracuse University out of 250 applicants in 1972.

Ten Conditions for New Discovery: From a Primary Major Work in 1976 to the 2010 Nobel Prize

—When, around, was your work first recognized as involving a world-class achievement?

Well, my first major scientific work emerged in 1976, or about 4 years after I moved to Syracuse University. Building upon the work of Professor Kohei Tamao, of Kyoto University in Japan, I discovered that nickel could be used as a catalyst to significantly enhance the progress of desired organic reactions. Dr. Tamao published an article on nickel complex-catalyzed cross-coupling reactions of Grignard reagents containing Mg in 1972. I consider his work to be a Nobel Prize-class accomplishment. We then became the first researchers in the world to report that aluminum and other metals could be successfully used with retention of regiochemistry and stereochemistry, the use of palladium catalysts being particularly favorable. I believe that the use of palladium rather than nickel as a catalyst was critical to our success.

—Was it by a type of *serendipity* that you came to utilize palladium?

I do not totally refute the involvement of serendipity in research, although I must say that I place serendipity as one of the less significant conditions needed to make epoch-making discoveries. I firmly believe that *systematic exploration* is the core of new scientific discoveries, which I feel I owe to the experience of working alongside and discussing matters with Professor Brown. Systematic exploration cannot take place overnight. It instead requires years or even decades of the tireless efforts and pursuits. First come *needs* and *desires*, or the goals of research achievement. Plans that are based on those needs and desires must be developed. Systematic exploration must then proceed alongside the above-mentioned *plans*. Systematic exploration must also be assisted by ample *knowledge*, appropriate *judgments*, and many innovative *ideas*. At the same time, systematic exploration requires firm belief with unshakable toughness that you will eventually succeed no matter how many times one may fail. You could refer to that as strong *will power* and *optimism*. You could then finally add *serendipity* to the above elements or factors. You would be very unlikely to succeed by merely doing things in an inconsistent, haphazard sort of way. Skillful researchers often produce unexpected, excellent achievements through sheer persistence that are contrary to their initial expectations. This might indeed be called the true essence of serendipity or joyful discoveries.

Expanding the Scope of Research to the Greatest Extent Possible

—You have focused for 50 years on research in a single area to make a difference.

Yes, but although my research interests may seem to have been centered around a single theme I do organize my projects to have a wide range of applicability; I often advise my students and staff members to avoid narrowly limiting the scope of their research when selecting research topics. I typically suggest that they set a wide range of goals rather than merely focusing on a single reaction or compound. I always consider it better to aim at exploring, you could say, something wider and deeper than aiming at the individual compound level.

For example, I like to encompass the entire combination of, for example, 10 or so organic compound-building elements and 60 or so usable metallic elements, when designing a research project involving organometallic chemistry. I believe that researchers should be sufficiently aggressive in expanding the scope of their research to the greatest extent possible. After all, it is completely free of charge and requires very little time to create research strategies within your mind.

Ultimate Research Goals-New Conceptual Insights

—What advice would you like to give to MANA and other young researchers?

Without neglecting the significance of individual research targets in your current research projects you should remain fully aware of the ultimate goals of what you are trying to achieve in the long run in your research program. And developing new insights into the conceptual framework of the research you are engaged in is very important in fulfilling that purpose. For example, the Russian scientist Dmitri Mendeleev identified the concept of quantum chemistry even before the discipline had actually been developed, and his work indeed provided the atomic basis needed to understand chemistry. He argued that the atomic weight of an element gets increased by a single unit when a proton or neutron is added. He also reasoned that the number of electrons should equal that of the protons in order for the atom to be electrically neutral. These conceptual insights then led him to identifying the presence of then unknown elements and the eventual formulation of the periodic table.

Dr. Negishi (leftmost) accompanying Prof. Brown (rightmost) during a visit to Stockholm to attend the 1979 Nobel Prize Award Ceremony.

—MANA is pursuing international research cooperation. What do you consider to be the most important in promoting international projects?

Overcoming language barriers and other critical issues contributes to the enhancement of international partnerships. And aside from language communication skills I believe it to be important that researchers receive help in developing a healthy sense of self-esteem that their level of academic performance or excellence is at the one in a thousand, or at least several hundred, level. When I look back on my personal experience I remain certain that one of the key qualifications needed by young scientists is to excel in fair academic competition. I consider a key prerequisite to success to be being able to positively appraise one's own abilities and values in a competitive environment.

A total of around 400 postdoc researchers worked in Professor Brown's laboratories, including Professor Akira Suzuki and myself. Arithmetically, it means that the rate of winning Nobel Prizes by H.C. Brown associates has been one in 200.

—What are your plans for the near future?

I announced before receiving the Nobel Prize that I would semi-retire at the age of 75. It is common at Purdue for professors to fully retire 5 years after making this announcement. I was originally planning to retire at the age of 80, but shortly after receiving the Nobel Prize, I was offered the position of the founding director of the Negishi-Brown Catalytic Research Institute, which was to be newly created at Purdue University. My role as the director will commence soon, and I am looking forward to receiving applications from all the excellent researchers spread across the globe.

—Thank you for taking the time to hold this interview and sharing some very interesting stories and thoughts.

Sustained Research in Japan Gains Recognition

Dmitri Golberg
MANA Principal Investigator,
Nano-Materials Field

CONVERGENCE interviewed Dr. Dmitri Golberg, a MANA Principal Investigator who has as his research forte the synthesis and analysis of inorganic nanotubes (NTs) and related nanomaterials made with such compounds as BN, ZnO, and ZnS, these having been found second best after CNTs/graphenes as suitable for nanotech applications. He received the Third Thomson Reuters Research Front Award 2012 for outstanding contributions to the field of Materials Science, with Dr. Yoshio Bando, for work on "Novel Syntheses of One-Dimensional Inorganic Nanomaterials and their Applications."

—Could you describe the awarded research to our readers?

Dr. Bando and I, as well as the talented post-docs and others with our group, had been working not only on one-dimensional but also two-dimensional nanomaterials in terms of using transmission electron microscopy to make physical property measurements of "nanoinorganics", in my case looking not only at ZnO and ZnS which actually were in the center of the awarded research but also at BN, MoS_2, WS_2 and many others However, it is the steady flow over a continuous period of papers, like over a decade's time, in recognized journals which seems to have attracted the attention of Thomson Reuters. They use some sort of formula, checking the amount of citations and correlated statistics, to see who should be recognized as being the "researcher in front" … . But again, I would like to say that we as a group produced the results that gained the award for NIMS.

—The award means that you have been recognized as a leading researcher in the Materials Science field in Japan. How do you feel about this?

This is a credit to NIMS/MANA. I was able to carry out work here because of the affiliation which enabled me to be settled down, along with the latest equipment that could only be utilized at a few locations elsewhere around the globe. The objective of this research also means studying future use of semiconducting wide bandgaps in nanostructures. We have many "clever people" so we should be able to surpass the competition for this research field, like use of deep ultraviolet.

—What was your motivation to come to research in Japan?

I came to Japan in 1993, to make a first post-doc … I did not expect to stay on in Japan for this long, but the science funding status then was quite difficult in Russia, in comparison with Japan where one could enjoy the funding and other opportunities availed. Actually, I had been here at "NIMS" from before the merger of the two institutions which brought forth NIMS in 2001, doing research work both at NIRIM (the inorganics research institute) and NRIM (the metals research institute). Now I am a permanent person here, and I much enjoy the current situation. I see no reason why I should move elsewhere.

—How do you think about research environment at MANA, in particularly compared with those at oversea institutes?

My counterparts overseas are envious of the research environment here. It is not only unique in that there are so many foreigners accessing Japan's technology base but I like the fact that I can hire up to three excellent post-docs to assist my work – fortunately, the institution has a great reputation and many attractive features that help bring in researchers from inside Japan as well as from abroad. Having the best talent pool, via former researchers who have now gone on to become full professors and can arrange to have the most intelligent of their students come join us, also helps. We have new state-of-the-art equipment to carry out research at the leading edge. As an aside, for young researchers, being able to rub shoulders with Nobel Laureates on visit to MANA in Tsukuba can be considered an exceptional way of motivating them.

—You are planning to start a joint research project with Russian institutes, is this correct?

Yes, there is some planned cooperation between NIMS and the National University of Science and Technology "MISIS" in Moscow. I actually graduated from this University many years ago but looking to be a "diplomat" of sorts – I am being asked to bring Japanese researchers into the SKOLKOVO (Russian "Silicon Valley") ambitious project also, being a Russian-born professor … I believe any good professor can help with international exchanges though, be a "diplomat" of sorts. I think if someone can bring the two countries closer in the science field, it could be me for the area of nanotechnology. The Russian side is spending much money now, including offering Mega-Grants to research nanotech.

—Could you please tell me about your future research plans as a leader of Nanotube Unit?

We hope to produce research people and results that will lead the way, a "nanofactory" of top-notch people and excellent research, producing good fundamental scientific results that will reflect upon nanotube studies. For the very near future though, we are focusing on measuring properties of nanomaterials. For this, we are using Transmission Electron Microscope (TEM) as a means of directly measuring electrical, mechanical and thermal properties for example. But opto-electronics is also now seen being useful in other types of research work. TEM could be used to manipulate the nanomaterials as well, like welding with an electron beam.

Dmitri Golberg

In 1995 the Russian became one of the first scientists to launch a full scale research on BN nanotubes. Since then he has become a world-recognized expert in this field and published more than 100 papers solely on this topic.

Construction of New Research Complex Complete —NanoGREEN / WPI-MANA Building

March 2012 witnessed the construction of a new multidisciplinary research complex at the NIMS Namiki site, and which was designed to be the new focal point of research on environmental energy technology and innovative materials development. The complex consists of two units—MANA's WPI-MANA building and the NanoGREEN building—with the area between the two buildings serving as a free space where researchers can meet and discuss their work. This article presents the environmental performance and workplace conditions of the new research complex, which intended for use as a world-class nanoarchitectonics research leader and promoting international research efforts.

Japan's First Practical Microgrid Power System

The complex is supplied with power by a de-centralized system that uses a combination of four different power sources: solar energy, storage batteries, an emergency generator, and the commercial power supply. It is basically Japan's first operating microgrid (smart grid) power system, and enables both amount of power consumed to be reduced and an uninterruptible power feed in a commercial power outage.

Environmentally-friendly Design and Construction

The new buildings were rated the highest grade of S by a government-led certification system that assesses the overall environmental performance of buildings. The construction work was designed to minimize any burden on the environment, and includes less CO_2 emissions and complete recycling of construction waste products.

Top-class Environmental Performance

A number of innovative environment-oriented technologies have been utilized in a variety of locations. Automatic control of the temperature, humidity, and luminance allow for a decrease in the necessary energy consumption but increased indoor comfort. By making maximum use of natural energy the new style of architecture will continue to be the world's leading zero-energy lab.

Water Cooling System

Stored rain water is sprinkled over the window panes to cool the building in summer.

Solar Panels

Solar panels were integrated into the building as part of the roofing materials. In addition, solar panels were also installed as window roofs connected to the pane glass.

Sun Shielding Louvers

Louvers filter all the direct sunlight while scattering the daylight in thereby indirectly distributing it.

Comfortable and Exciting Meeting Place

The complex provides an excellent research environment with an increased level of comfort, and meeting spots that enhance communication and interactions taking place between researchers. All the office and lab areas, as well as the corner of the atrium, which was designed to serve as an academic 'melting pot,' are barrier-free.

Academic Melting Pot

The hallways connecting the two buildings were developed to be open areas in thus stimulating personal interactions taking place between researchers of different academic and cultural backgrounds.

Auditorium

Through being equipped with a full-scale screen and the latest audiovisual apparatus the 97-seat tiered auditorium enhances active discussion during workshops, seminars, and conferences.

Full-height Windows Along the Corridors

All the researchers' activities in the lab are open to being viewed externally. The office areas are also lined with glass windows—an environment that is open to communication.

Cafeteria

The cafeteria, named the 'Melting Pot Cafe,' provides a casual place for both national and international researchers and company engineers to meet and greet.

Principal Investigator Offices

On each floor several researchers of different expertise share the same space in thereby fostering collaborations and creative ideas.

Highly Efficient Photoenergy Conversion Based on Surface Nanoarchitectonics

Kohei UOSAKI
MANA Principal Investigator
Coordinator of Nano-Green Field

Solar energy attracts much attention as a renewable energy source. However, there is great gap in time and region between the solar energy supply and energy consumption and, therefore, solar energy must be converted to electricity or chemical energy for storage and transportation. In this respect, many research groups are working on artificial photosynthesis mimicking natural photosynthesis, in which high energy compounds are efficiently synthesized utilizing photoexited electrons as many functional molecules are arranged in highly order manner. We are trying to achieve highly efficient conversion of photoenergy to electricity and chemical energy at metal and semiconductor surfaces, on which functional molecules are arranged in order. Here two examples are introduced.

In the first example, we have achieved highly efficient conversion of visible light to electricity by modifying a gold surface by porphyrin (sensitizer) - ferrocene (electron relay) - thiol (surface attaching group) linked molecule. However, the limited absorption of visible light by porphyrin limits overall efficiency. Recently we demonstrated that photoenergy conversion efficiency can be dramatically enhanced by placing gold nanoparticle on top of the molecular layer as an optical antenna so that photon is collected effectively.

Second example is photoelectrochemical hydrogen production and CO_2 reduction by utilizing photoabsorption by semiconductor Si. If semiconductor is illuminated with light of sufficient energy, electron is excited from the valence band to the conduction band, leaving hole in the valence band. Theoretically water electrolysis and CO_2 reduction can be achieved only by light but actual efficiency is quite low because reactivity (catalytic activity) of semiconductor surface is generally low. We recently achieved highly efficient photoelectrochemical hydrogen generation at Si(111) surface by introducing viologen layer as an electron transfer mediator and platinum complex as a hydrogen evolution catalyst on the surface by multistep surface reactions. Detailed in situ determination of interfacial structure during hydrogen evolution reaction proved that the Pt complex acts as "confined molecular catalyst" for hydrogen evolution reaction. This electrode shows also high efficiency and selectivity for CO_2 reduction in contrast to the result at Pt metal electrodes.

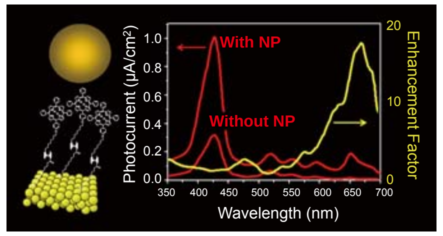

Figure 1. Wavelength dependencies of photocurrent with and without gold nanoparticle photo antenna and enhancement factor at gold electrode modified with porphyrin-ferrocene-thiol linked molecule.

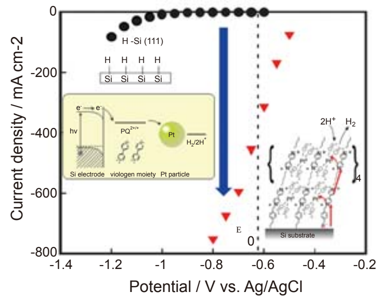

Figure 2. Potential dependence of photocurrent due to hydrogen evolution reaction at hydrogen terminated and viologen layer/Pt complex modified Si(111) electrode and a proposed model.

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Development of Thermoelectric Materials: Atomic Structure Level, Grain-size Level

Takao MORI
Group Leader
MANA Scientist
Nano-Materials Field

Only one third of all primary energy consumed, namely oil, coal, gas is effectively used, with much being lost as waste heat. Thermoelectric (TE) materials which can convert waste heat to electricity through the Seebeck effect, can have huge benefit for society. We aim to develop TE materials viable for wide spread application, through a multifaceted approach based on control on the atomic structure level and grain-size level.

Traditional TE materials have been composed of elements like Bi, Te, Pb which are not in the "element strategy". We focus on atomic clusters and network-like structures as a way to highly functionalize inorganic materials composed of common safe elements. Through bridging sites, we have been able to obtain striking physical properties, though it is still on the level of serendipity. We have discovered the long awaited n-type counterpart to p-type boron carbide, which is one of the few TE materials previously commercialized. We are also developing a silicon-based cage compound with high TE performance and high temperature oxidation resistance.

Developing methods to control thermal conductivity is important not just for TE but also for thermal management. We focus on several novel mechanisms on the atomic structure level (Fig. 1), such as the "Symmetry Mismatch Effect", which we propose is a mechanism when the particular symmetry of the building blocks of the crystal structure has a large mismatch with the crystal symmetry.

On the other hand, control on the grain-size level, namely, nano/microstructure control is also very important. We have been trying to utilize additives/sintering aids by using knowledge gained from structural materials, although such additives have traditionally been avoided in TE research. We have discovered the zinc additive method, wherein, silicon aggregations in borosilicides were removed, improving the crystallinity (Fig. 2), and enhancing TE performance. In general, control of the grain structure leads to control of the phonon scattering on the grain boundaries, making it a powerful tool to decrease thermal conductivity.

One recent discovery which well illustrates the high potential of network materials is our discovery (patent submitted and paper in preparation) of a material where the network is composed mainly of a common safe element, and where with the same crystal structure and same component elements, we are able to control p-n characteristics freely and obtain absolute values of Seebeck coefficients larger than 200 μV/K for both p and n. This discovery is another huge step forward toward the development of viable thermoelectric materials for wide scale application.

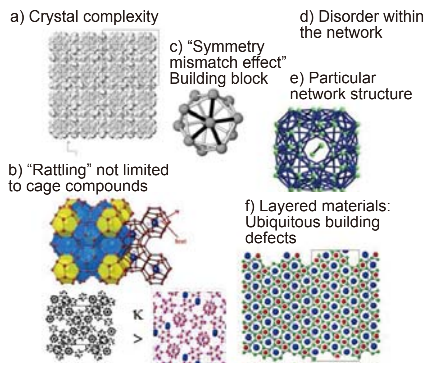

Figure 1. Mechanisms for thermal conductivity control

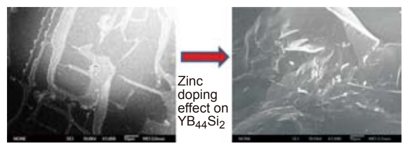

Figure 2. Zinc doping effect

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Smart Biomaterials to Control Stem Cell Differentiation
- Designing Instructive Scaffolds for Cardiac Tissue Engineering -

Giancarlo FORTE
MANA Scientist
Nano-Bio Field

The use of stem cells for cardiac tissue regeneration is a challenging opportunity for the setup of innovative, minimally invasive strategies to treat diseases for which a therapy is not currently available (Figure 1).

Recently, the sensitivity of undifferentiated and mature cells to the mechano-physical properties of the surface they adhere to and grow on has been documented, while the molecular processes leading to the transformation of these feelings in a biological response remain largely unknown. Unraveling the mystery behind the molecular processes by which stem cells decipher substrate nanostructure and respond by selectively activating a specific genetic program would be of invaluable help to design bio-inspired materials and thus to treat cardiac pathologies. In principle, a cardiac-specific scaffold should be able to comply with cardiac muscle architecture, be deformable as to indulge and possibly sustain cardiac contraction. It should also favor stem cell electromechanical coupling with host tissue, while promoting the vascularization of the newly-formed tissue (Forte et al., 2011).

To get an insight in stem cell response to material mechano-physical properties, we developed an original approach based on the use of smart biomaterials. Poly-ε-caprolactone (PCL) layers displaying different overall stiffness values but similar chemical composition were obtained by cross-linking tetra-branched PCL with acrylate end-groups in the presence of linear PCL telechelic diacrylates. These surfaces show a peculiar nano-structure that can be easily tuned, thus allowing the control of stem cell fate without using biological factors. A high throughput strategy has been applied to study stem and cardiac cell gene expression in response to changes in surface mechano-physical features. By this means, we highlighted a different sensitivity of human stem cells and contractile cells to substrate stiffness, as demonstrated by cell adhesion rate and the formation of the adhesion processes on different stiffness. More importantly, a marked effect of substrate elasticity on stem cell and contractile cell phenotype was demonstrated by PCR arrays. The elucidation of the molecular processes guiding stem cell mechano-sensitivity could lead to the preparation of novel patient-specific, tissue-targeted engineering products.

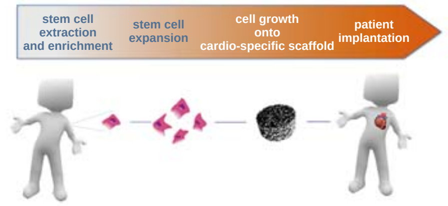

Figure 1. Autologous cardiac-specific bio-substitutes can be prepared culturing patient stem cells on instructive scaffolds.

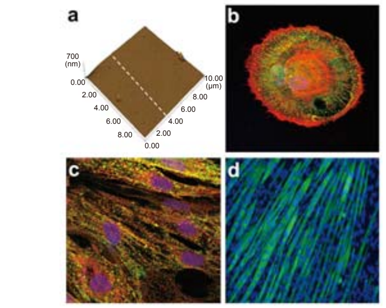

Figure 2. Differential response of stem and differentiated cells to nano-structured biomaterials (a). The image shows the morphology of a single human mesenchymal stem cell (b), as compared to mature cardiomyocytes (c) or myotubes obtained from skeletal muscle resident progenitor cells (d) and grown onto polymeric films with controlled stiffness and nano-structure.

Reference
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Charge-free Reverse Wormlike Micelles: Self-assembly beyond Conventional Common Sense

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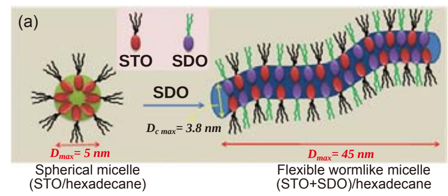
Surfactants are amphiphilic molecules and so can form a variety of self-assembled structures in water or oil or in both. They may form normal micelles, liquid crystals of different geometries, vesicles, and also reverse micelles. Just above the critical micelle concentration (*cmc*) surfactant molecules self-assemble into spherical micelle, which can grow into cylinder or wormlike (entangled) under certain condition of temperature, composition, or upon addition of salts or cosurfactants. Self-assembly in aqueous medium has been extensively studied and together with theoretical development have enabled us to anticipate the possible self-assembled structures of amphiphiles judging from their molecular architecture. However, self-assembly in nonaqueous media has not been so well studied and free structure control of reverse micelles is still a challenging task.[1] Reverse micelles are composed of hydrophilic polar core and lipophilic nonpolar shell, i.e., the structure of reverse micelles is opposite to that of conventional micelles in aqueous systems. Reverse micelles have been utilized as a micro/or nanoreactor for several aqueous chemical reactions and have also been templated in tailored synthesis of nanoparticles utilizing their various geometries.

Despite the tremendous applications in solubilization, separation and extraction, drug delivery, material synthesis, etc, formulation of charge-free reverse wormlike micelles (a network structure) without incorporation of water has been an up-hill challenge for the last few decades. Recently, we succeeded in the formulation of a novel charge-free nonionic reverse wormlike micelle in organic liquid.[2] This route involves the addition of sucrose dioleate (SDO) to the semi-dilute reverse micellar solutions of sucrose trioleate (STO) in hexadecane. We noted that less lipophilic nonionic surfactant SDO promotes one-dimensional growth to STO reverse micelles and leads to the formation of transient networks of viscoelastic reverse wormlike micelles. The zero-shear viscosity increases by ~ 4 orders of magnitude, and it is the mixing fraction of SDO to STO that determines the rheology of the system.

The proposed system is unique and is far from common sense in this field. Normally for surfactant self-assembly the co-presence of polar and nonpolar solvent is usual and strong amphiphilicity of surfactant with bearing charge is common. Therefore, the present system appears not to be common sense in terms of conventional surfactant science. However, such an unusual system would be highly interesting from viewpoint of practical application were one could avoid both charge and water.



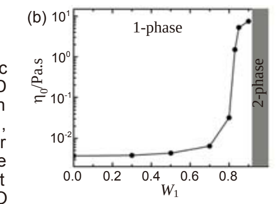


Figure. (a) Schematic representation of 1D micellar growth in nonaqueous media, and (b) zero-shear viscosity and phase behavior against weight fraction of STO in total system [W_1 = SDO/(STO + SDO)]. Note that STO alone forms spherical micelle in hexadecane. Less lipophilic nonionic surfactant SDO, which does not form any structure in hexadecane can be solublized at the palisade layer of STO micelles and as a result, the curvature decreases favoring micellar growth.

References
1. Shrestha, L. K., *et al., Langmuir*, **27**, 5862-5873(2011).
2. Shrestha, L. K., *et al., Langmuir*, **27**, 2340-2348(2011).