

Dr. Hiroshi Masuhara is one of the most reputable Japanese chemists, awarded The Purple Medal (紫綬褒章) and The Order of Sacred Treasure, Gold Ray with Double Neckless (瑞宝中綬章), honored internationally The Porter Medal (corresponding to Nobel Prize in photochemistry), and Academicians of The Royal Academy of Belgium and National Academy of Sciences India. This is due to his pioneering study on nano/micro molecular systems exploring their new photochemical and photophysical phenomena by developing time-resolved spectroscopy, imaging, and manipulation methods and by elucidating their dynamics and mechanism. He has opened new interdisciplinary area of molecular photo-science, whose results are published as ~560 papers, ~120 reviews, and ~20 books. His pioneering works have attracted many young researchers and graduate students. Now 63 doctors graduated/educated from Masuhara Laboratory/Project and 40 researchers coached in Masuhara Project are working in the relevant areas of molecular photo-science as professors and distinguished researchers in 10 countries including Taiwan.

This long developing academic research by Dr. Masuhara before shifting to NCTU in 2008 is summarized as “**Laser Nano Chemistry: Methodology and Molecular Nano Dynamics**”. This consist of 3 parts.

### 1) Laser Nano Spectroscopy and Nano Photochemistry

Photophysical and photochemical dynamics of nano-crystals, nm-thin films and nm-surface/interface layers of solids were measured and analyzed with high energy and temporal resolutions similar to those in solution. Ultrafast intersystem crossing, charge separation, exciplex formation, and photothermal heating processes characteristic of the “solid” state were elucidated and first reported by the Masuhara group for aromatic molecules, dyes, EDA complexes, TiO<sub>2</sub>, polymers, and resists. Spectroscopy of single nanoparticles was examined as functions of their shape, size, morphology, internal structure, and environment. **Novel nm size effects on aromatic/polymer crystals and polymer nanospheres were investigated and their origins were confirmed to be structural confinement, namely, size-dependence of crystal lattice softening, molecular packing, and polymer conformation.** These novel effects are characteristic of molecular material, and completely different from well-known nm size effects of semiconductors and metals which are due to electron confinement.

### 2) Laser Nano Manipulation and Chemistry of Photon Pressure

A focused near-infrared laser beam exerts mechanical force, called as photon pressure, on nanomaterials, enabling their trapping and manipulation. The optical trapping studies have been conducted mostly by physicists and optical engineers, while its extension to chemistry was started by the Masuhara group. By examining various polymer and supramolecular systems, Dr. Masuhara elucidated, for the first time, **molecular structure-photon pressure relation which opens a new field that could be coined “chemistry of photon pressure”.** This is further being extended to trapping dynamics of single nanoparticles in solution at room temperature. He also developed a method of 3-dimensional trapping and manipulation of nanoparticles and applied it to fix the nanoparticles onto a substrate. **The nanoparticles were freely patterned with resolution of a few ten nm in solution.** Although the spatial resolution is less than that of the 2-dimensional surface manipulation by a STM tip at low temperature under vacuum, much broader applicability is very important for semiconductors, metal nanoparticles, biological material, cells, and protein crystals.

### 3) Laser Nano Ablation: Dynamics and Bio Application

Intense pulsed laser excitation of nano-sized droplets, aggregates, crystals, powders, and films generates high density excited states and intermediates. Their mutual interactions

and their successive absorption of excitation photons lead to ablation, expansion and subsequent contraction, surface protrusion, and so on. The Masuhara group developed time-resolved imaging methods to probe laser-induced morphological dynamics and combined them with the time-resolved spectroscopy. They extended systematic studies on nanosecond-, picosecond, and femtosecond laser ablation and related phenomena and determined rates of expansion, surface roughening, ablation, and contraction. They demonstrated how electronic excitation of molecules in solids evolves and leads to morphological changes. Based on these results, **molecular mechanisms of laser ablation was proposed; cyclic multiphotonic absorption mechanism for ns-excitation and a transient pressure mechanism due to very rapid electronic-vibrational energy conversion for fs-excitation.** All the processes are within the framework of a classic Jablonski diagram without additional states and intermediates such as plasma. Hence laser ablation and related dynamics are now understood as typical nonlinear photochemical phenomena.

By utilizing the transient pressure induced by fs-excitation, Masuhara and his colleagues unraveled novel laser ablation phenomena and developed new methodologies. Femtosecond multiphoton excitation of molecular films gives discrete and multistep etching, fs ablation of microcrystals in solution gives **the smallest nanocrystal of a dye with the diameter of 13 nm by top-down method, and the shockwave induced by transient pressure can manipulate individual living cells from a substrate without damage.** Dr. Masuhara also succeeded in the preparation of proteins crystals with **high quality** and their model compounds by introducing femtosecond pulse into supersaturated protein solution. In addition, they succeeded in controlling the crystal growth with femtosecond multiphoton excitation. These results have important implications in the area of bioscience.

Prof. Masuhara was invited as a Chair Professor of NCTU in April 2008 and stayed in NCTU since then. **Key research results of his Laser Bio/Nano Science Laboratory in DAC NCTU** are classified into the below 3 topics. **The research was carried out under the strong support of ATU (Aiming Top University) Project of MOE** and published as ~100 papers and presented as ~100 invited lectures.

### **1) Laser Trapping-Induced Molecular Crystallization and Crystal Growth**

Dr. Masuhara and his group first demonstrated laser trapping-induced crystallization

ahead of the world. They have studied systematically sequential behavior of nucleation, growth, and dissolution of amino acids and a protein. Here one representative example of L-phenylalanine plate-like crystal is described. **Its crystal is prepared by a focused continuous-wave near-infrared laser beam even in unsaturated solution upon the laser irradiation into the air/solution interface.** One single crystal is generated from the focus and continuously grows two-dimensionally while being trapped by the laser. The crystal growth is stopped when the laser power is decreased. The crystal size is kept constant for a certain time period, and then the crystal starts dissolution. The growth and dissolution processes are directly followed under microscope and their rates are determined. Based on such approach Dr. Masuhara and his members concluded that **amino acid crystal is prepared and surrounded by a highly concentrated domain of a few hundreds of micrometers consisting of amino acid liquid-like clusters.** This crystallization mechanism receives much attention as a seminal proposal from NCTU and many international collaborations with Hokkaido and Saitama universities, Tokyo Institute of Technology, and Nara institute of Science and Technology have been carried out being supported by ATU Project.

## **2) Femtosecond Laser Trapping and Ejection of Dielectric Nanoparticles**

We have found a novel trapping and ejection phenomenon of nanoparticle characteristic of femtosecond laser trapping in solution, which has never been reported by CW laser trapping. The nanoparticles are trapped at the focus and then a rapidly and asymmetrically alternative nanoparticle ejection is observed as perpendicular to the linear laser polarization. Since that, a series of nanoparticles trapping experiments, such as dependences of laser polarization, pulse width and nanoparticle density, have been investigated in detail to elaborate this phenomenon. We propose that the unique directional ejection is due to the formation of strongly packed nanoparticle assembly during fs laser irradiation. In order to confirm the mechanism, we used different nanoparticles, chemically modified the surface of nanoparticles, introduced a fluorescent probe dye into the surface, and systematically extended experimental research. Trapping well generated by femtosecond laser beam that attracts and gathers nanoparticles repetitively. Inside the trapping well due to an intense femtosecond light field, the hydrophobic surface of nanoparticles enables the formation of an asymmetric assembly. Scattering and gradient forces are induced and once the scattering force overcomes the

trapping force, the assembly is ejected out to the surrounding. It is worth noting that the assembly was directly observed after being ejected under a certain condition. Their conclusion that **a strongly packed assembly of nanoparticles are fabricated by femtosecond laser pulse indicates a new potential methodology of light assisted assembling of molecules and nanoparticles.**

### **3) In-situ Patterning and Controlling of Living Cells by Femtosecond Laser**

Femtosecond laser ablation induces bubbling in solution and a formed bubble expands rapidly from the focus to the outside. This expansion generates supersonic jet loading mechanical force on living cells and tissues located around the focus. The target cells are not directly irradiated, so that their photochemical damages are not induced. Further femtosecond laser ablation has superior features due to its photomechanical mechanism, leading less decomposition at the focus too. This laser ablation bubbling method was combined with photochemically and photothermally modified surface patterns, and novel control of living cells was achieved. Femtosecond laser ablation of physiological solutions generates shockwave and cavitation bubbles, and living cells are mechanically manipulated in solution and patterned on the modified surface of a glass. **Femtosecond laser ablation fabricating cytophobic and cytophilic domains enable us to form living cell patterns and to study cell migration and cell–cell interaction.** This method will be one of possible useful methods to construct future living cell tips and devices. The experimental studies were carried out under collaboration with Prof. F.-J.Kao of NYMU and Profs. Y.-K. Li and F.-Y. Hsu of NCTU, and also Prof. Y. Hosokawa of Nara Institute of Science and Technology.

## **CURRICULUM VITAE of Dr. Hiroshi MASUHARA**

Born in Tokyo on March 29, 1944 as a son of Ryoji and Midori MASUHARA

### **Education**

Ph. D., in chemistry, Osaka University with Prof. Noboru Mataga (1971)

Mc. D., in chemistry, Tohoku University with Prof. Masao Koizumi (1968)

B. A., in chemistry, Tohoku University with Prof. Masao Koizumi (1966)

### **Academic position**

Chair Professor, National Chiao Tung University (2008-present)

Chief Scientist, Hamano Life Science Research Foundation (2007-2008)

Professor Emeritus, Osaka University (2007-present)

Professor, Osaka University (1991-2007)

Professor, Kyoto Institute of Technology (1984-1991)

Research Associate, Osaka University (1972-1984)

Postdoctoral Fellow, Osaka University (1971-1972) with Prof. Noboru Mataga

### **Academy Members**

Foreign Fellow of National Academy of Sciences, India (2010-present)

Foreign Member of Royal Flemish Academy of Belgium (1998-present)

### **Society Fellows and Honored Doctor**

Emeritus member of Japanese Society of Molecular Science (2019 - present)

Emeritus member of Japanese Photochemistry Association (2017 - present)

The Chemical Society of Japan Fellow (2010-present)

IUPAC Fellow (2007 - 2011)

Doctor Honoris Causa de Ecole Normale Supérieure de Cachan, France (2006-2013)

### **Highly Ranked Governmental Awards (Emperor of Japan)**

The Order of the Sacred Treasure, Gold Rays with Neck Ribbon (2017), 瑞宝中綬章

The Purple Ribbon Medal (2008), 紫綬褒章

### **Scientific Awards and Prizes**

Asian and Oceanian Photochemistry Association Award (2010)

Mizushima-Raman Lectureship, JSPS-India DST (2010)

Mukai Prize (2010)

Outstanding Scholar Award of Foundation for the Advancement of Outstanding Scholarship, Taiwan (2008)

Spectroscopic Society of Japan Award (2006)

Porter Medal (European, American and Asian Photochemistry Association) (2006)

The Chemical Society of Japan Award (2006)

Kenjiro SAKURAI Memorial Award, Optical Industrial Technology Development Association (2005)

Osaka Science Prize (1994)

Divisional Award of the Chemical Society of Japan (1994)

Moet Hennessy Louis Vuitton International Prize "Science for Art" Excellence de Da Vinci, France (1993)

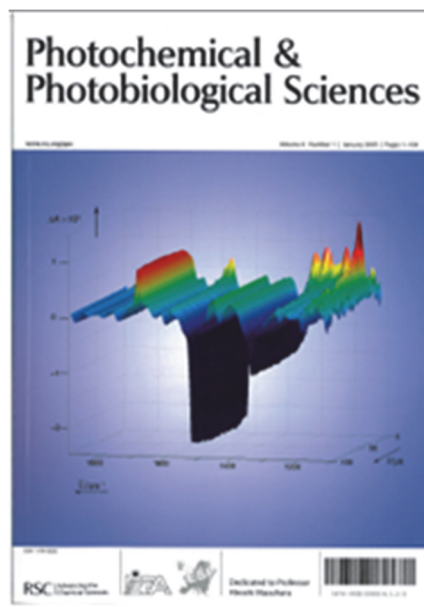
Japanese Photochemistry Association Award (1989)

### **Society Honor**

Masuhara Lectureship Award was started in Asian and Oceanian Photochemistry Conference (2012 - present)

Hiroshi Masuhara Festschrift of **J. Phys. Chem. C**, American Chemical Society (2009)

Hiroshi Masuhara Special Issue of **Photochemical and Photobiological Sciences**, Royal Society of Chemistry (2005)



### **Director of Group Research Project**

Research Supervisor, PRESTO Project “Innovative Use of Light and Materials/Life”, JST (Japan Science and Technology Agency) (2008-2015)

Project Director of Grand-in-Aid for Scientific Research on Innovative Area “Molecular Nanodynamics”, Japanese Society for Promotion of Science (JSPS) (2004-2007), ~1x 10<sup>9</sup> JPY

Project Director of Grand-in-Aid for Scientific Research on Innovative Area “Single Organic Nanoparticle”, Japanese Society for Promotion of Science (JSPS) (1998-2001), ~5 x 10<sup>8</sup> JPY

Director, Masuhara Microphotoconversion Project, Exploratory Research for Advanced Technology Program, Research and Development Corporation of Japan (1988-1994), ~2 x 10<sup>9</sup> JPY

### **Professional Activity (Society President, Adviser, and Important Committee Member)**

Advisor for Australian Research Council Center of Excellence Project “Exciton Science” (2017-2022)



Advisor for Grand-in-Aid for Scientific Research on Innovative Area “Optical Manipulation of Nano Materials”, Prof. Hajime Ishihara Project Leader, Japanese Society for Promotion of Science (JSPS) (2016-2021)

Advisor for Grand-in-Aid for Scientific Research on Innovative Area “Photosynergetics”, Prof. Hiroshi Miyasaka Project Leader, Japanese Society for Promotion of Science (JSPS) (2014-2019)

Advisor for Institute of Molecular Science, Okazaki, Japan (2013 - 2015)

Advisor for Grand-in-Aid for Scientific Research on Innovative Area “Dynamic Ordering & Integrated Functions”, Prof. Koichi Kato Project Leader, Japanese Society for Promotion of Science (JSPS) (2013-2018)

Advisor for Grand-in-Aid for Scientific Research on Innovative Area “Strong Light-Matter Interaction”, Prof. Hiroaki Misawa Project Leader, Japanese Society for Promotion of Science (JSPS) (2007-2011)

Committee Member of INPAC Program, Katholieke Universiteit Leuven, Belgium (2007 - 2010)

Executive Committee Member of Chemical Society of Japanese (2007 - 2009)

Associate Member of Science Council of Japan (2006-2012)

Committee Member of Nano Program, Royal Dutch Academy (2003)

Committee Member of IAP Program, Ministry of Education of Belgium (2002 - present)

President of Asian and Oceanian Photochemistry Association (2002 - 2004)

President of Japanese Photochemistry Association (2000 - 2001)

Member of IUPAC Photochemistry Commission (1998 - 2001)

Executive Committee Member of Japanese Applied Physics Society (1997 - 2001)

Executive Committee Member of Japanese Photochemistry Association (1992 - 1995, 1998 - 2000)

**22 Guest Professorships in Japan, Taiwan, France, Belgium, China, and USA (IBM)**

**Editor, Editorial Board, and Advisory Board Members in 15 Journals**

<b>Organization of Conference, Workshop, Seminar, and Summer Course</b>
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Dr. Masuhara and young professors of DAC NCTU **Annually Organize Summer Course and Workshop from 2012 to 2018**. They invited 20 Japanese, 3 American, and 3 Belgian Professors as lectures of the Tutorial Course, and the sum of the participants is now 723. In 2017 and 2018, 20 Japanese and about 10 non-Taiwanese graduate students joined us. The Workshop always follows the Summer Course where Japanese and Taiwanese (outside of NCTU) professors presented the adv