8th RSC-CSJ Joint Symposium 2017

—Recent Developments in Plasmonics—

March 18th (Sat), 2017

Hiyoshi Campus, Keio University; Yokohama, Kanagawa, Japan

The Chemical Society of Japan & The Royal Society of Chemistry

The 8th RSC-CSJ Joint Symposium

—Recent Developments in Plasmonics—

The Chemical Society of Japan　The 97th Annual Meeting

■Date　March 18th (Sat), 2017　9:00-17:20

■Venue　S3; Room J29,　Room J29, House B, Bldg., 4
Hiyoshi Campus, Keio University; Yokohama, Kanagawa, Japan

■Hosted by
The Chemical Society of Japan (CSJ) & The Royal Society of Chemistry (RSC)

■ 9:00	*Opening Remarks*	**Robert Parker** CEO; RSC	
■ 9:10	*Recent Developments in Plasmonics: Introduction*	**Hiromi Okamoto** Institute for Molecular Science	…1
■9:20	*Site-selective Nanoscale-polymerization via Plasmon Induced Charge Separation*	**Yukina Takahashi** Kyushu University	…3
■10:00	*Investigating Functional Materials using Surface Plasmon Resonance Spectroscopy*	**Petra J Cameron, et al.** University of Bath	…5
■10:40	**Break**		
■10:50	*Spectral Properties of Plasmon-Molecule Hybrid States and Coupled Plasmonic Systems*	**Kosei Ueno, et al.** Hokkaido University	…7
■11:30	*Metamaterials for Reactive Plasmonic Applications*	**Wayne Dickson, et al.** King's College London	…9
■12:10	**Lunch Break**		
■13:30	*Space and Temporal Properties of Plasmons in a Single Metal Nanoplate Revealed by Scanning Near-field Optical Microscopy*	**Kohei Imura** Waseda University	…11
■14:10	*Photonics at the Biomedical Interface: Intracellular Surface-enhanced Raman Spectroscopy*	**Sumeet Mahajan** University of Southampton	…13
■14:50	**Break**		
■15:10	*Alloy Plasmonic Materials for Sensor Applications*	**Yoshiaki Nishijima** Yokohama National University	…15
■15:50	*Chemical Applications of Nanophotonic: Probing the Structure of Soft Matter with Chiral Nanostructures*	**Malcolm Kadodwala** University of Glasgow	…17
■15:50	*Plasmonic Optical Tweezer toward Molecular Manipulation*	**Yasuyuki Tsuboi** Osaka City University	…19
■17:10	*Closing Remarks*	**Hisashi Yamamoto, President,** CSJ	

Welcome to Japan!

Dear Colleagues

Globalization is the process of international integration arising from the interchange of world views, products, ideas, and other aspects of culture.

Particularly, collaborations between chemists of various countries often transcend borders and cultural differences. The fundamental nature of chemical science allows chemists to communicate using knowledge of their field. Its focus is on chemistry students and chemists interested in developing a global approach to open new science and technology, by participating in an international symposium. Overall, multidisciplinary is the password for the successful globalization of chemistry.

The Chemical Society of Japan (CSJ) is delighted to be co-organizing with the Royal Society of Chemistry (RSC) at the occasion of 97th Annual Meeting of Chemical Society of Japan at Yokohama. I am confident that multidisciplinary research can be developed through these international symposia.

I would like to thank Dr. Robert Parker, Chief Executive Officer, Dr. Kathleen Too, International Development Manager-Asia and Dr. Hiromitsu Urakami, Representative of Japan office of RSC, and Prof Hiromi Okamoto and Prof. Yasuyuki Tsuboi, representing CSJ as Chairs, for their great effort to make RSC-CSJ joint symposium possible.

Mutual exchange and collaboration among chemists between two countries have continued ever after, even when the flow of knowledge became no longer one-sided, as it was in early days, and have led to tremendous contributions to the development of new chemistry.

It is our great pleasure and honor to add new pages to the history of mutual exchange between global countries.

Professor Hisashi Yamamoto

President;

The Chemical Society of Japan

Welcome Address

Dear Colleagues

It is my pleasure to welcome you to the 8th UK-Japan Symposium, one of a series of joint events held by the Royal Society of Chemistry and our long-standing partner the Chemical Society of Japan.

We have worked closely with the Chemical Society of Japan for a number of years to support scientific collaboration and exchange between our two countries. In 2010 we formalised our relationship by signing an international cooperation agreement, which we renewed in 2015.

The theme for this year's symposium is Fundamentals and Chemical Applications of Plasmonics and it brings together leading Japanese and UK scientists to discuss their latest research. We hope that the presentations will stimulate the exchange of ideas and experiences between all participants and we thank each of the speakers and all the participants for their contributions to this symposium.

We are very grateful to the Chemical Society of Japan, Professor Hiromi Okamoto and Professor Yasuyuki Tsuboi for their organisation of this symposium and we look forward to continuing to work even more closely together in the future.

Once again a very warm welcome to what promises to be an exciting scientific event. I hope that today offers an opportunity to build relationships and find new opportunities for researchers from the UK and Japan to collaborate on this important topic.

I wish you all an informative, productive and enjoyable day.

Dr Robert Parker
Chief Executive Officer
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Hiromi Okamoto

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➢ Educational Background

1983 B.Sc., The University of Tokyo
1985 M.Sc., School of Science, The University of Tokyo
1993 Doctor of Science, The University of Tokyo

➢ Professional Career

1985 Research Associate, Institute for Molecular Science
1990 Research Associate, The University of Tokyo
1993 Associate Professor, The University of Tokyo
2000 Professor, Institute for Molecular Science

➢ Research Interests

1) Near-field microscopy and nano-optics, plasmons
2) Chiral spectroscopy/microscopy

➢ Awards

2012 The Chemical Society of Japan Award for Creative Work

➢ Recent Publications

1. "Nonlinear optical effects in trapping nanoparticles with femtosecond pulses", Yuqiang Jiang, Tetsuya Narushima, Hiromi Okamoto *Nat. Phys.* **2010,** *6*, 1005.
2. "Anomalous light transmission from plasmonic capped nano-apertures", Kohei Imura, Kosei Ueno, Hiroaki Misawa, Hiromi Okamoto *Nano Lett.* **2011,** *11*, 960.
3. "Local Optical Activity in Achiral Two-Dimensional Gold Nanostructures", Shun Hashiyada, Tetsuya Narushima, Hiromi Okamoto *J. Phys. Chem. C* **2014,** *118*, 22229.
4. "Circular Dichroism Microscopy Free from Commingling Linear Dichroism via Discretely Modulated Circular Polarization", Tetsuya Narushima, Hiromi Okamoto *Sci. Rep.* **2016,** *6*, 35731.

Recent Developments in Plasmonics: Introduction

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Collective oscillation modes of conduction electrons in metallic materials, known as plasmons, generate huge polarisations on the materials. Plasmons couple with electromagnetic waves and localises in the vicinities of the metal surfaces, to form resonance states (surface plasmon resonance) that depend on the materials, shapes and sizes of the substances. Surface plasmon resonance is the origin of unique optical properties of metal nanostructures, that is, localisation of the optical field into nano-spaces and huge local field enhancement, and in conjunction with them, reduction of the light velocity in the vicinity of the metal surface, resulting in an increase in wave number (i.e., spatial frequency). In the field of chemistry, a variety of surface enhanced spectroscopies have been developed on the basis of plasmon resonances for nearly 40 years, which provide fundamental techniques of chemical sensors. In addition, it has been recently reported that plasmon resonances accelerate photochemical reaction processes. In the fields of applied physics and optics, the unique optical characteristics of plasmons are exploited as the bases for metamaterials with negative refractive index and various novel optical elements including light sources. Studies pursuing the fundamental characteristics of plasmon resonances and studies on fabrication of metal nanoparticles that yield various unique characteristics are also being made continuously.

In this symposium, we have invited 9 researchers from Japan and UK who are active at the forefront of these fields. The lectures cover research fields from fundamental to application studies, that is, plasmon-assisted chemical reactions (Takahashi), characterization of materials with plasmon resonance spectroscopy (Cameron), strong coupling between plasmons and molecules (Ueno), optical characteristics of plasmon-based metamaterials (Dickson), near-field imaging of plasmons (Imura), biomedical application of surface enhanced Raman spectroscopy (Mahajan), application of plasmons to sensors (Nishijima), chiral plasmonics (Kadodwala) and optical manipulation with plasmons (Tsuboi). With this series of lectures, we intend to overview the current status of researches on plasmons in chemistry and new developments in the future.

I am grateful to Prof. Y. Tsuboi and Prof. M. Kadodwala who co-organised this symposium.

Yukina Takahashi

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➢ Educational Background

2002 B.Eng., The University of Tokyo (supervisor: Prof. Noritaka Mizuno)
2004 M.Eng., Graduate School of Engineering, The University of Tokyo (supervisor: Prof. Tetsu Tatsuma)
2007 Doctor of Engineering, Graduate School of Engineering, The University of Tokyo (supervisor: Prof. Tetsu Tatsuma)

➢ Professional Career

2007 Project research associate, Institute of Industrial Science, The University of Tokyo
2010 Assistant professor, Faculty of Engineering, Kyushu University

➢ Research Interests

1) Photoelectrochemistry
2) Energy conversion
3) Plasmonic metal nanoparticles

➢ Awards

2006 The Predoctoral Fellowship, Hayashi Memorial Foundation for Female Natural Scientists
2011 Excellent Oral Presentation Award for Young Scientist, The 30th meeting of Solid Surface Photochemistry
2012 MMS Award, Precious Metals Research Grants of TANAKA Holdings
2013 Hot Article Award Analytical Sciences (Vol.29, No.1), "Gold Nanorods Embedded in Titanium Oxide Film for Sensing Applications", The Japan Society for Analytical Chemistry
2014 Yang Researcher Award of The Electrochemical Society of Japan (Sano Award), The Electrochemical Society of Japan

➢ Recent Publications

1. "Site-selective Nanoscale-polymerization of Pyrrole on Gold Nanoparticles via Plasmon Induced Charge Separation",
   Y. Takahashi,* Y. Furukawa, T. Ishida, and S. Yamada *Nanoscale* **2016,** *8*, 8520.
2. "Thermal and Chemical Stabilization of Silver Nanoplates for Plasmonic Sensor Application",
   Y. Takahashi,* K. Suga, T. Ishida, and S. Yamada* *Anal. Sci.* **2016,** *32*, 275.
3. "Metal and Metal Oxide Nanoparticles for Photoelectrochemical Materials and Devices",
   Y. Takahashi,* S. Yamada, and T. Tatsuma *Electrochemistry* **2014,** *82*, 730.
4. "Gold Nanorods Embedded in Titanium Oxide Film for Sensing Applications",
   Y. Takahashi,* N. Miyahara, and S. Yamada* *Anal. Sci.* **2013,** *29*, 101.

Site-selective Nanoscale-polymerization via Plasmon Induced Charge Separation

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Metal nanostructures, such as gold and silver nanoparticles, can generate strong enhanced electromagnetic fields in nanospaces around the surfaces by coupling with incident light in the wavelength region of visible to near-IR on the basis of localized surface plasmon resonance (LSPR). They can be applied to enhancement of both absorption and emission processes of the light-absorbing molecules and/or semiconductors placed in the nanospaces. It is also known that noble metal nanoparticles combined with an n-type semiconductor, such as TiO_2 and ZnO, exhibit plasmon induced charge separation (PICS).[1,2] When the resonant light irradiates plasmonic metal nanoparticles on an n-type semiconductor, electrons of the metal nanoparticles transfer to the semiconductor resulting in reductive and oxidative reactions on the surfaces of the semiconductor and the metal nanoparticles, respectively. This phenomenon can be utilized to various applications, such as visible-light responsive photocatalysts, photovoltaic cells, and sensing devices.

Control of space arrangement between dye molecules and metal nanostructures is very important for effective utilization of LSPR, because optical properties of dye molecules which only exist at strong enhanced electric fields can be enhanced. In addition, oxidative reactions based on PICS are expected to proceed site-selectively at strong enhanced electromagnetic fields on the surface of metal nanoparticles. Therefore, in this symposium, site-selective nanoscale-polymerization of monomeric dye molecules, such as pyrrole, based on PICS using gold nanoparticle (AuNP)-loaded TiO_2 system (Figure 1)[3] is demonstrated. Detailed mechanisms of polymerization reactions will be discussed.

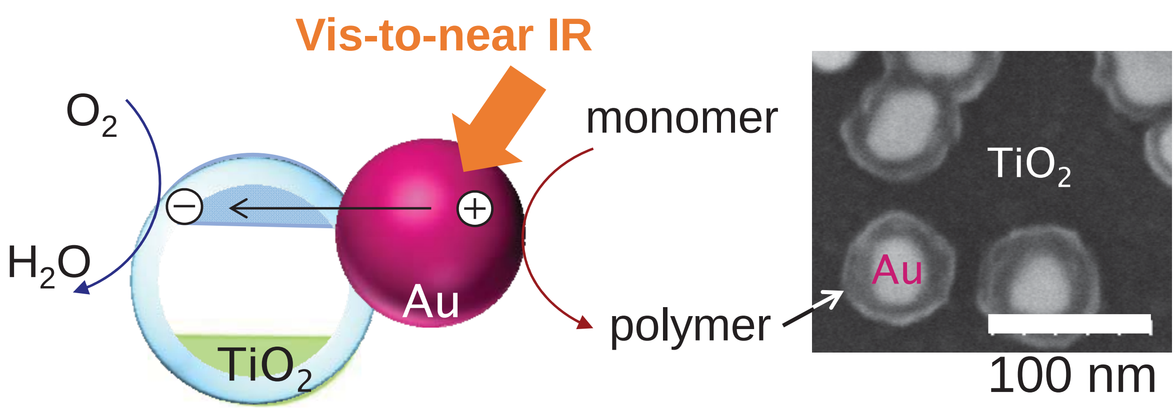

Figure 1. A schematic illustration and a scanning electron microscopic image of the site-selective nanoscale-polymerization based on PICS.

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2. T. Tatsuma, *Bull. Chem. Soc. Jpn.*, **2013**, *86*, 1.
3. Y. Takahashi, Y. Furukawa, T. Ishida, S. Yamada, *Nanoscale*, **2016**, *8*, 8520.

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➢ Educational Background

1996 –2001 Masters of Chemistry. Department of Chemistry, University of Edinburgh, UK.

Research Project: "Electropolymerisation of conducting polymers".1998

2001 –2004 PhD, University of Bath (Supervisor Prof. L. M. Peter)

➢ Professional Career

2005 –2007, Alexander Von Humboldt Research Fellow, Max Plank Institute for Polymer Research, Mainz, Germany.

2007-2011 RCUK Research Fellow, University of Bath, UK

2012-2014 Assistant Professor, University of Bath, UK

2014-present Associate Professor, University of Bath, UK

➢ Research Interests

1) Energy Materials
2) Functional Materials
3) Solar Cells and Fuel Cells

➢ Awards

Harrison-Meldola Memorial Prize and Medal (Royal Society of Chemistry, 2009)

➢ Selected Publications

1. 'Can slow-moving ions explain hysteresis in the current–voltage curves of perovskite solar cells?', Giles Richardson, Simon E. J. O'Kane, Ralf G. Niemann, Timo A. Peltola, Jamie M. Foster, Petra J. Cameron, Alison B. Walker, *Energy Environ. Sci.*, **2016**, *9*, 1476.
2. 'Cs^+ incorporation into $CH_3NH_3PbI_3$ perovskite: substitution limit and stability enhancement', Niemann, Ralf G; Gouda, Laxman; Hu, Jiangang; Tirosh, Shay; Gottesman, Ronen; Cameron, Petra J; Zaban, Arie; *J. Mater. Chem. A*, **2016**, *4*, 17819.
3. 'Polymerization of low molecular weight hydrogelators to form electrochromic polymers',
4. Peter S. Kubiak, Salmah Awhida, Christopher Hotchen, Wentao Deng, Ben Alston, Tom O. McDonald, Dave J. Adams, Petra J. Cameron, *Chem. Commun.*, **2015**, *51*, 10427.
5. 'A simple approach for the fabrication of perovskite solar cells in air', Simone Casaluci, Lucio Cina, Adam Pockett, Peter S. Kubiak, Ralf G. Niemann, Andrea Reale, Aldo Di Carlo, P. J. Cameron, *J. Power Sources*, **2015,** *297*, 504.
6. 'Electrochemically-triggered spatially and temporally resolved multi-component gels', Jaclyn Raeburn, Ben Alston, Jeanne Kroeger, Tom O. McDonald, Jonathan R. Howse, Petra J. Cameron, Dave J. Adams, *Mater. Horiz.* **2014**, *1*, 241.

*A full list of my publications can be found at http://people.bath.ac.uk/chppjc/publications.html

Investigating Functional Materials using Surface Plasmon Resonance Spectroscopy

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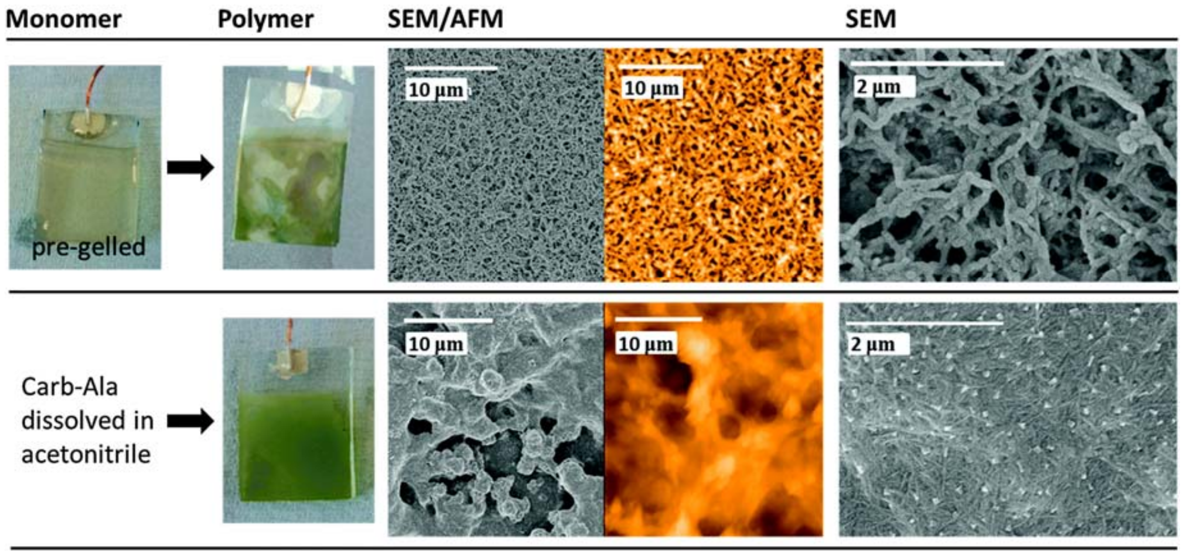
In our research we use surface plasmon resonance spectroscopy (SPR) and optical waveguide spectroscopy (OWS) to investigate the formation and function of a range of soft and hard materials. We combine electrochemistry with SPR to allow the in-situ surface triggered self-assembly of dipeptides into hierarchically structured hydrogels. Using SPR allows us to probe the kinetics of gel formation and the layer-by-layer deposition of ultrathin gel layers with different functionality. We have shown that we can electropolymerise hydrogels in situ to make electrochromic polymers. Polymers prepared from pre-formed gels have quite different micro-structures to polymers formed from monomers dissolved in solution. In the group we also have a strong focus on energy materials. We have used OWS to measure dye uptake in dye sensitized solar cells; more recently we have also been using OWS to look at degradation in perovskite films for perovskite solar cells.



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➢ Educational Background

1999 B.Sc., Faculty of Science, Hokkaido University
2001 M.Sc., Graduate School of Science, Hokkaido University
2004 Doctor of Science, Graduate School of Science, Hokkaido University

➢ Professional Career

2004-2006: JSPS Research Fellow, Hokkaido University
2006 -2007: Research Assoc., Hokkaido University
2007-2008: Assist. Prof., Hokkaido University
2007-2014: PRESTO Researcher, Japan Science and Technology Agency
2008-2009: Specially-Appointed Assoc. Prof., Hokkaido University
2009-present: Assoc. Prof., Hokkaido University
2010-2012: Visiting Associate Professor, Institute for Molecular Science

➢ Research Interests

1) Photochemistry on Nanostructured Surface
2) Plasmon-Based Physics and Chemistry

➢ Awards

2011 The Japan Chemical Society Award for Young Chemist, The Chemical Society of Japan
2010 The Japanese Photochemistry Association Prize for Young Scientist, Japan Photochemistry Association
2007 Yong Scientist Prize, Japan Soc. Analytical Chemistry

➢ Recent Publications

1. "Surface plasmon optical antennae in the infrared region with high resonant efficiency and frequency selectivity" K. Ueno, Q. Sun, M. Mino, T. Itoh, T. Oshikiri, H. Misawa, *Opt. Express* **2016**, *24*, 17728.
2. "Surface-enhanced terahertz spectroscopy using gold rod structures resonant with terahertz waves", K. Ueno, S. Nozawa, H. Misawa, *Opt. Express* **2015**, *23*, 28584.
3. "Plasmon-assisted water splitting using two sides of the same SrTiO3 single-crystal substrate: Conversion of visible light to chemical energy", Y. Zhong, K. Ueno, T. Oshikiri, H. Misawa et al., *Angew. Chem. Int. Ed.* **2014**, *53*, 10350.
4. "Plasmon-enhanced photocurrent generation and water oxidation from visible to near-infrared wavelengths", K. Ueno, H. Misawa, *NPG Asia Mater.* **2013**, *5*, e61 (2013).
5. "Surface plasmon-enhanced photochemical reactions", K. Ueno, H. Misawa, *J. Photochem. Photobiol. C*, **2013**, *15*, 31.
6. "Homogeneous nano-patterning using plasmon assisted photolithography", K. Ueno, S. Takabatake, K. Onishi, H. Itoh, Y. Nishijima, H. Misawa, *Appl. Phys. Lett.* **2011**, *99*, 011107. Highlighted in Nature Photonics (News & Views). *Nat. Photonics*, **2011**, *5*, 517.

Spectral Properties of Plasmon-Molecule Hybrid States and Coupled Plasmonic Systems

Kosei Ueno,[a] Sho Nozawa,[a] Han Yu,[a] Jie Li,[a] Quan Sun,[a] Tomoya Oshikiri,[a] and Hiroaki Misawa[a,b]
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We are studying plasmon-based chemistry through utilizing well-defined metallic nanostructures fabricated by advanced nanofabrication technologies. To construct metallic nanostructures array with a strong enhancement of electromagnetic field for the photochemical reaction fields, the near field coupling between adjacent metallic nanostructures is often employed for localizing electromagnetic field at the nanogap and inducing dark states of quadrupole mode which shows longer plasmon dephasing. In addition, the strong coupling between plasmon and exciton is also utilized for the modulation of electronic states and the enhancement of light matter coupling. So far, the spectral properties based on the couplings have been mainly studied through far field extinction or reflection spectroscopy. However, it is still unclear that hybrid states are really formed due to the couplings only by measuring the far field spectrum because the spectrum modulation is also induced by the interference of their spectra. Here, we report on the spectral properties of plasmon-molecule hybrid states and coupled plasmonic systems by measuring excitation spectrum or near field spectrum to confirm the formation of hybrid states.

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2. K. Ueno, S. Nozawa, H. Misawa, *Opt. Express* **2015**, *23*, 28584.
3. H. Yu, Q. Sun, K. Ueno, T. Oshikiri, A. Kubo, Y. Matsuo, H. Misawa, *ACS Nano*, **2016**, *10*, 10373.

Wayne Dickson

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➢ Educational Background

1998 B.Eng., Mechanical Engineering, Queen's University Belfast
2001 B.Sc., Department of Physics, Queen's University Belfast
2005 Doctor of Physics, Department of Physics, Queen's University Belfast (supervisor: Prof. A. Zayats)

➢ Professional Career

2005 Queens University Belfast (PD)
2010 King's College London (PD)
2012 Lecturer, King's College London

➢ Research Interests

1) Nanophotonics, metmaterials.
2) Nanofabrication, self-assembly.

➢ Recent Publications

1. "Bulk plasmon - polaritons in hyperbolic nanorod metamaterial waveguides", Vasilantonakis N, Nasir ME, Dickson W, Wurtz GA, Zayats AV. *Laser Photon. Rev.* **2015**, *9(3)*, 345.
2. "Hyperbolic polaritonic crystals based on nanostructured nanorod metamaterials", Dickson W, Beckett S, McClatchey C, Murphy A, O'Connor D, Wurtz GA, Pollard R, Zayats AV. *Adv. Mater.* **2015**, *27(39)*, 5974.
3. "Hydrogen detected by the naked eye: optical hydrogen gas sensors based on core/shell plasmonic nanorod metamaterials", Nasir ME, Dickson W, Wurtz GA, Wardley WP, Zayats AV. *Adv. Mater.* **2014**, *26(21)*, 3532.

Metamaterials for Reactive Plasmonic Applications

Wayne Dickson,[a] Mazhar Nasir,[a] Pan Wang,[a] Emiliano Cortes,[b] William Wardley,[a] Margoth Cordova-Castro,[a] Stefan Maier,[b] Anatoly Zayats[a]
[a]*Department of Physics, Nano-optics and plasmonics, King's College London, U.K.*
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Plasmonic metamaterials have long been viewed as excellent candidates as optical sensors due to their strong light matter interaction[1] and high sensitivity to variations in the local refractive index[2]. Self-assembled metamaterials based on arrays of quasi-ordered metallic nanorods possess the necessary sensitivity combined with a scalable fabrication approach.[2] These materials have already demonstrated the ability to detect bio-chemical events,[2] ultrasound[3] and more recently, hydrogen[4] with high sensitivity making them excellent candidates for modern sensors. Furthermore, the flexibility of this metamaterial platform make it an excellent candidate for the development of electro-optical sensors based on functionalised quantum tunnelling junctions. In this paper I will review these developments and present the prospects for future sensors and devices.

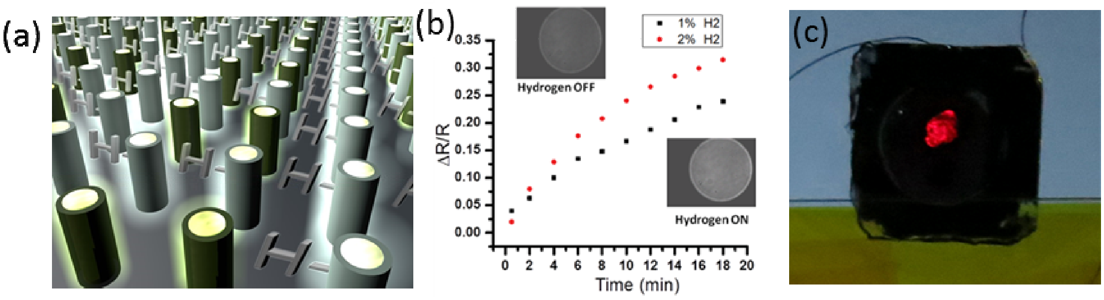

Figure 1. (a) Schematic of hydrogen sensor comprised of core(Au)/shell(Pd) nanorods. (b) Change in reflectivity of an Au/Pd metamaterial on exposure to 2% H_2 in N_2. (c) Light emission from a tunneling-electron-driven metamaterial (the size of the emission area is approximately 2mm^2).

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3. V. V. Yakovlev, W. Dickson, A. Murphy, J. McPhillips, R. J. Pollard, V. A. Podolskiy, A. V. Zayats, *Adv. Mater.*, **2013**, *25*, 2351.
4. M. E. Nasir, W. Dickson, G. A. Wurtz, W. P. Wardley, A. V. Zayats, *Adv. Mater.*, **2014**, *26*, 3532.

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➢ Educational Background

1995 B.Sc., Osaka University (supervisor: Prof. Toshio Kasai)
1997 M.Sc., Graduate School of Science, Osaka University (supervisor: Prof. Toshio Kasai)
2000 Doctor of Science, Graduate School of Science, Osaka University (supervisor: Prof. Toshio Kasai)

➢ Professional Career

2000 JSPS research fellow (PD), Tohoku University
2001 Assistant professor, Institute for Molecular Science
2009 Associate professor, Waseda University
2015 Professor, Waseda University

➢ Research Interests

1) Plasmonics
2) Nanomaterials
3) Near-field optics

➢ Awards

2005 Japan Society for Molecular Science Award for Young Scientists
2007 The Spectroscopical Society of Japan Award for Young Scientists
2007 The Chemical Society of Japan Award for Young Chemists
2012 The Young Scientists' Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology

➢ Recent Publications

1. "Raman Activity and Dynamics of Plasmons on a Rough Gold Film Studied by Ultrafast Scanning Near-Field Optical Microscopy", K. Imaeda, K. Imura. *ACS Book Series "Frontiers of Plasmon Enhanced Spectroscopy"*, **2016**, *2*, 121.
2. "Photobleaching-Assisted Near-Field Absorption Spectroscopy: Its Application to Single Tubular J-Aggregates", K. Imura, H. Mizobata, Y. Makita. *Bull. Chem. Soc. Jpn.*, **2016**, *89*, 1518.
3. "Multiple Resonances Induced by Plasmonic Coupling between Gold Nanoparticle Trimers and Hexagonal Assembly of Gold-Coated Polystyrene Microspheres", T. Uchida, Y. Yoshikawa, M. Tamura, T. Iida, K. Imura. *J. Phys. Chem. Lett.*, **2016**, *7*, 3652.
4. "Dye-assisted Visualization of Plasmon Modes Excited in Single Gold Nanoplates", K. Imaeda, K. Imura. *Chem. Phys. Lett.*, **2016**, *646*, 179.
5. "Observation of Plasmon Wave Packet Motions via Femtosecond Time-resolved Near-field Imaging Techniques", Y. Nishiyama, K. Imura, H. Okamoto. *Nano Lett.*, **2015**, *15*, 7657.

Space and Temporal Properties of Plasmons in a Single Metal Nanoplate Revealed by Scanning Near-field Optical Microscopy

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Plasmon excited in metal nanoparticle confines optical fields spatially as well as temporally, and generates enhanced fields in the vicinity of the particle. The enhanced fields have attracted much attention due to their potential use in metamaterials, chemical sensing,[1,2] and photochemical reactions. To design plasmonic optical fields for the practical applications, spatio-temporal properties of the plasmon should be revealed. Since the spatial scale of the plasmon is smaller than the diffraction limit of light, the microscope with a nanometer spatial resolution is indispensable for visualization.[3] We developed various types of near-field imaging methods to study static and dynamical properties of the plasmons in the metal nanoparticles.[4-6] In this symposium, we present spatio-temporal properties of plasmons excited in a single metal nanoplate.

Figure 1(a) and 1(b) shows spatial distributions of optical fields on a single gold nanoplate visualized by detecting two-photon photoluminescence from gold. In Fig.1(a), the optical field is enhanced at the apex of the plate due to the lightning rod effect and/or a dipolar mode excitation. In Fig. 1(b), on the other hand, the optical field is enhanced not only at the apex but also at the internal sites of the plate. The spatial features in Fig. 1(b) originate from dipolar and quadrupolar plasmon mode excitations. We examined temporal properties of the plasmons, and found that dynamics on the plate in Fig. 1(a) is almost identical regardless of the internal position of the sample, whereas that in Fig. 1(b) is position dependent. Plasmons provide novel photochemical processes at the nanometer scale, and thus the knowledge obtained from the near-field imaging techniques are indispensable for the applications of the plasmonic optical fields.

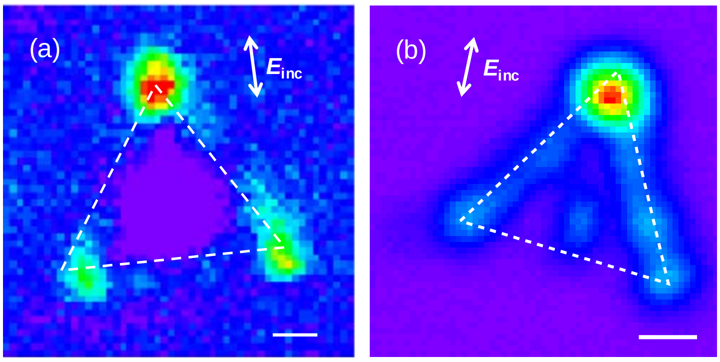

Figure 1(a), **1**(b) Two-photon excitation images of single gold nanoplates obtained by detecting visible photoluminescence from the sample. Excitation wavelength: ~800 nm. White dotted line: approximate shape of the nanoplate. Scale bars: 200 nm.

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Sumeet Mahajan

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➢ Educational Background

1998 M. Sc. Chemistry, Indian Institute of Technology Kanpur (supervisor: Prof. T. K. Chandrashekhar)
2005 M. Tech., School of Bioscience & Bioengineering, Indian Institute of Technology Bombay (supervisor: Prof. A. Q. Contract, Prof. S. Mukherji)
2008 Doctor of Philosophy, School of Chemistry, University of Southampton (supervisor: Prof. Phillip N. Bartlett)

➢ Professional Career

1999 Scientist, Defence R & D organisation
2008 Post-Doctoral Research Fellow, Cavendish Laboratory, University of Cambridge
2010 EPSRC Fellow, Department of Genetics, University of Cambridge
2012 Senior Lecturer/Associate Professor, University of Southampton

➢ Research Interests

1) Surface-enhanced spectroscopies
2) Label-free chemical imaging
3) Spectroscopic and imaging applications in biomedicine

➢ Awards

1998 Proficiency Prize, Indian Institute of Technology Kanpur
2008 Ronald Belcher Memorial Award by the RSC
2011 Raymond & Beverly Sackler Fellowship, Magdalene College, University of Cambridge

➢ Recent Publications

1. "Characterization and visualization of vesicles in the endo-lysosomal pathway with surface-enhanced raman spectroscopy and chemometrics", A. Huefner, W. L. Kuan, K. H. Müller, J. N. Skepper, R. A. Barker, S. Mahajan. *ACS Nano*, **2016**, *10(1)*, 307.
2. "Raman spectroscopy and coherent anti-Stokes Raman scattering imaging: Prospective tools for monitoring skeletal cells and skeletal regeneration", C. C. Moura, R. S. Tare, R. O. C. Oreffo, S. Mahajan. *J. R. Soc. Interface*, **2016**, *13*, 10.
3. "Observing Single Molecules Complexing with Cucurbit[7]uril through Nanogap Surface-Enhanced Raman Spectroscopy", D. O. Sigle, S. Kasera, L. O. Herrmann, A. Palma, B. De Nijs, F. Benz, S. Mahajan, J. J. Baumberg ,O. A. Scherman, *J. Phys. Chem. Lett*., **2016,** *7*, 704.
4. "Single nanoparticle-based heteronanojunction as a plasmon ruler for measuring dielectric thin films", L. Li, T. Hutter, W. Li, S. Mahajan. *J. Phys. Chem. Lett.*, **2015**, *6*, 2282.

Photonics at the Biomedical Interface: Intracellular Surface-enhanced Raman Spectroscopy

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Our research is at the interface of photonics, nanomaterials and biomedicine.[1-3] I will give an overview of the interdisciplinary work in my group but focus the talk on the applications involving plasmonics for biomedical spectroscopy. Here the research aim is to gain an understanding of biochemical phenomena inside cells and especially obtain information that cannot be provided by prevalent biological techniques. We use the highly sensitive molecular 'finger-printing' technique of surface-enhanced Raman spectroscopy (SERS) which relies on the plasmonic enhancement of signals from nanoscale metallic materials. In the case of biological cells we have used gold nanoparticle probes that are voluntarily taken up by them. We use the reporter-free SERS approach. Thus, the SERS nanoprobes report the immediate chemical environment around them. This SERS nanoparticle probe approach is made even more powerful by the functionalization of nanoparticles making them biocompatible as well as allowing the targeting of different organelles. We have shown that such biochemical information provided by SERS allows distinction between closely related cell types and between diseased and healthy cells.[4] Additionally the rich molecular information, available through the reporter-free SERS approach, harvested by multivariate methods allows distinction of organelles such as vesicles in the endolysosomal pathway inside cells.[5] We have further utilized this extremely sensitive methodology for monitoring uptake of small molecules (such as therapeutic drugs) inside organelles in live cells. This paves the way for measuring the bioavailability of drug molecules inside cells, which will improve cell-based assays and the drug discovery process. Although this highly sensitive, real-time chemical sensing capability is unparalleled by any other technique further developments in nanomaterials for SERS are expected to further strengthen this strategy and its adoption in biomedical research and drug discovery.

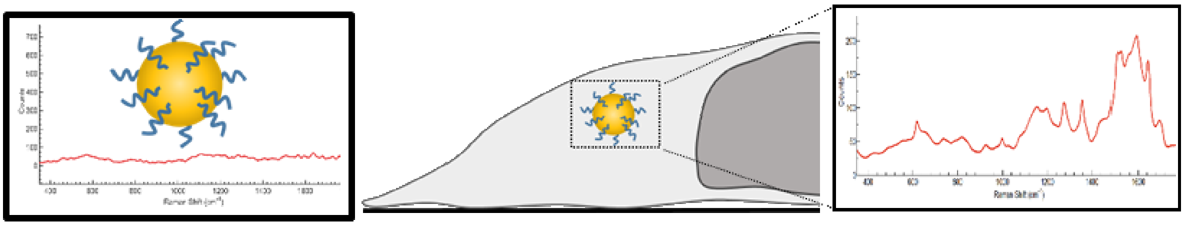

Figure 1. The Reporter-free SERS approach for obtaining chemical information inside cells.

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1. "Nanoparticles and intracellular applications of surface-enhanced Raman spectroscopy", J. Taylor, A. Huefner, L. Li, J. Wingfield, S. Mahajan, *Analyst*, **2016**, *141*, 5037.
2. "Visualizing electromagnetic fields at the nanoscale by single molecule localization", C. Steuwe, M. Erdelyi, G. Szekeres, M. Csete, J. J. Baumberg, S. Mahajan, C. F. Kaminski, *Nano Lett.*, **2015**, *15*, 3217.
3. "Tracking adipogenic differentiation of skeletal stem cells by label-free chemically selective imaging", J. P. Smus, C. C. Moura, E. McMorrow, R. S. Tare, R. O. C. Oreffo, S. Mahajan, *Chem. Sci.*, **2015**, *6*, 7089.
4. "Intracellular SERS nanoprobes for distinction of different neuronal cell types", A. Huefner, W. L. Kuan, R. A. Barker, S. Mahajan, *Nano Lett.*, **2013**, *13*, 2463.
5. "Characterization and visualization of vesicles in the endo-lysosomal pathway with surface-enhanced raman spectroscopy and chemometrics", A. Huefner, W. L. Kuan, K. H. Müller, J. N. Skepper, R. A. Barker, S. Mahajan, *ACS Nano*, **2016**, *10*, 307.

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➢ Educational Background

2004 B.Sc., Hokkaido University (supervisor: Prof. Noboru Kitamura)
2006 M.Sc., Graduate School of Science, Hokkaido University (supervisor: Prof. Noboru Kitamura)
2009 Graduate school of information science and engineering, Hokkaido University. (supervisor: Prof. Hiroaki Misawa)

➢ Professional Career

2008 – 2010 JSPS research fellowship for young scientist.
2010 – 2011 Post-doctoral researcher in Research Institute for Electronic Science, Hokkaido University.
2011－2013 Assistant Professor in Graduate school of Engineering, Yokohama National University. Principle investigator for Plasmonics lab.
2013－present Associate Professor in Graduate school of Engineering, Yokohama National University. Principle investigator for Plasmonics lab.

➢ Research Interests

YN is currently interested in the field of plasmonics and nano-photonics. Especially he is interested in the fabricating new optical materials for chemical sensor using surface enhanced Raman and infrared absorption (SERS/SEIRA), photo-thermal photo-electric conversion applications. Recently YN and his group succeeded to reveal experimentally and theoretically that artificially random arrangement of gold nano-disc structures have quieted strong electro-magnetic field enhancement due to the scattering light in the plane. One of the random plasmonic work has published in the ACS photonics. This strong EM field enhancement is useful for the SERS sensors. YN's group also succeeded to constructing the mid infrared plasmon structures for SEIRA materials. And these materials were applied to the SEIRA gas sensor. These plasmonic materials are effective to reducing the optical pass and total sensor system size with increasing the sensitivity.

➢ Awards

2009 CSJ Hokkaido winter meeting, best presentation award

➢ Recent Publications

1. "Anti-reflective surfaces: cascading nano/micro-structuring," Y. Nishijima, R. Komatsu, S. Ota, G. Seniutinas, A. Balčytis, S. Juodkazis, *APL Photonics*, **2016**, *1*, 076104.
2. "Au－Ag－Cu nano-alloys: tailoring of permittivity," Y. Hashimoto, G. Seniutinas, A. Balčytis, S. Juodkazis, Y. Nishijima, *Sci. Rep.*, **2016**, *2*, 25010
3. "Tunable Raman selectivity via randomization of a rectangular pattern of nano-disks," Y. Nishijima, J. B. Khurgin, L. Rosa, H. Fujiwara, S. Juodkazis, *ACS photonics*, **2014**, *1* 1006.
4. "Scaling rules of SERS intensity," Y. Nishijima, Y. Hashimoto, L. Rosa, J. B. Khurgin, S. Juodkazis, *Adv. Opt. Mater.*, **2014**, *2*, 382.

Alloy Plasmonic Materials for Sensor Applications

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Precious metal alloys enables new possibilities to tailor materials for specific optical functions. Here we present a systematic study of the effects of a nanoscale alloying on the permittivity of Au-Ag-Cu metals at 38 different atomic mixing ratios. The permittivity was measured and analyzed numerically by applying the Drude model described below equation.

$$\varepsilon(\omega) = \varepsilon(\infty) - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \qquad (1)$$

where $\varepsilon(\infty)$ represents permittivity at the high frequency limit (infinity), ω_p is the plasma frequency, Γ is the damping constant, respectively. Both, optical spectra and XRD results point towards an equivalent composition-dependent electron scattering behavior. Correlation between the fundamental structural parameters of alloys and the resulting optical properties is elucidated.

Plasmonic properties of the Au-Ag-Cu alloy thin film (SPR) and nanoparticles (LSPR) were investigated by numerical calculations. Sensing ability to the refractive index sensing, electromagnetic field enhancement for the surface enhanced Raman spectroscopic application (Au-Ag system) and hydrogen storage alloy sensing (Au-Pd system) will be discussed in the presentation.

Guidelines for designing plasmonic response of nano- structures and their patterns are presented from the material science perspective.

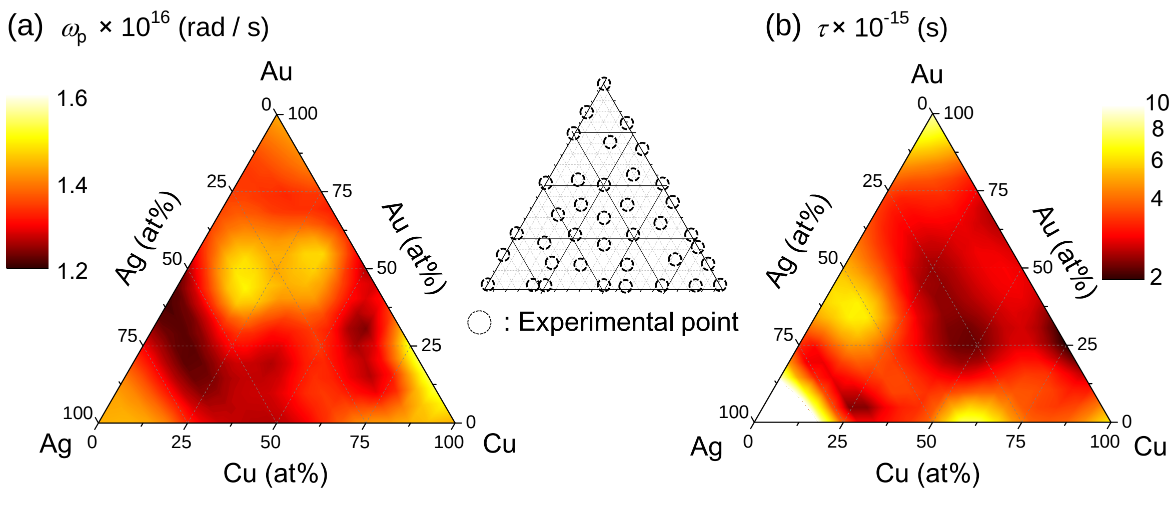

Figure 1. Interpolated ternary plots of experimentally obtained Drude parameters (a) plasma frequency ω_p and (b) relaxation constant τ. Middle inset indicates the atomic ratios at which experimental measurements were performed.

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➢ Educational Background

1994 PhD Chemistry, University of Nottingham, thesis Surface Science Studies of Model Adsorbates. Supervisor Prof Robert Jones.
1990 1st Class B.Sc. (Hons) Chemical Physics, University of Nottingham

➢ Professional Career

2016-Present Professor of Nanoscience and Nanotechnology, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ, UK
2013-2016 Reader, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ, UK
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1996-2007 Lecturer, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ, UK
1994-1995 Post-doctoral Fellow, FOM Institute

➢ Research Interests

1) Nanophotonics for Chemical Applications
2) Chirality

➢ Recent Publications

1. ‘Biomacromolecular stereostructure mediates mode hybridization in chiral plasmonic nanostructures’, Jack, C., Karimullah, A. S., Leyman, R., Tullius, R., Rotello, V. M., Cooke, G., Gadegaard, N., Barron, L. D., Kadodwala, M., *Nano Lett.*, **2016**, *16(9),* 5806.
2. ‘Spatial control of chemical processes on nanostructures through nano-localised water heating’ Jack, C. et al., *Nat. Commun.*, **2016**, *7*, 10946.
3. ‘Disposable plasmonics: plastic templated plasmonic metamaterials with tunable chirality’ Karimullah, A., Jack, C., Tullius, R., Rotello, V. M., Cooke, G., Gadegaard, N., Barron, L. D., Kadodwala, M., *Adv. Mater.*, **2015**, *27(37),* 5610.
4. ‘"Superchiral" spectroscopy: detection of protein higher order hierarchical structure with chiral plasmonic nanostructures’, Tullius, R., Karimullah, A. S., Rodier, M., Fitzpatrick, B., Gadegaard, N., Barron, L. D., Rotello, V. M., Cooke, G., Lapthorn, A., Kadodwala, M.,. *J. Am. Chem.Soc.(Commun.)*, **2015**, *137(26),* 8380.
5. ‘Scaling rules of SERS intensity’, Y. Nishijima, Y. Hashimoto, L. Rosa, J. B. Khurgin, S. Juodkazis, *Adv. Opt. Mater.*, **2014**, *2*, 382.

Chemical Applications of Nanophotonic: Probing the Structure of Soft Matter with Chiral Nanostructures

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Chirality, the property of an object to lack mirror symmetry and thus be able to exist in two non-superimposable mirror image forms, is a ubiquitous property in nature. Indeed, the building blocks of life, amino acids and sugars are chiral, and this sense of handedness propagates in to the complex structures of life. In this talk I will discuss how near fields with chiral asymmetries, generated by light scattering from chiral nanostructures, can uniquely characterise higher order biological structure which is invisible to conventional spectroscopy. I will demonstrate how the interaction of chiral nanostructures and biomaterials can be understood using concepts from physical chemistry and atomic and molecular physics; orbital hybridisation and quantum interference phenomenon such as electromagnetic induced transparency (EIT).

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Educational Background:
1990 Bachelor of Engineering,
Osaka University
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1995 Doctor of Engineering, Osaka University
(Department of Applied Physics, School of Engineering)

Professional Career:
1995-1996: Fuji PhotoFilm Co. Ltd.
1996 -1999: Research Associate, Kyoto Institute of Technology.
1999-2001: Assistant Prof & Lecturer., Kyoto Institute of Technology.
2001 – 2013: Associate Prof., Hokkaido University.
2013 ~ present: Professor, Osaka City University (current position)

1998-2001: Researcher JST, PRESTO (area of "Structure and Transformation")
2001-2004: Head of SORST project (JST).
2004 ~ present: Laser System Inc. Ltd. Technical Advisor
2010 ~ 2014: Researcher JST, PRESTO (area of "Photoenergy Conversion Systems")

Research Interests:
Laser Chemistry, Microspectroscopy, Plasmonics, Laser micro/nano-Processing, Polymer Dynamics

Selected Publications

1. "Metallic-Nanostructure-Enhanced Optical Trapping of Flexible Polymer Chains in Aqueous Solution as Revealed by Confocal Fluorescence Microspectroscopy", M. Toshimitsu, et al., Y. Tsuboi, *J. Phys. Chem. C*, **2012**, *116(27)*, 14610.
2. "Reversible Photoinduced-Formation and Manipulation of a Two-dimensional Closely Packed Assembly of Polystyrene Nanospheres on a Metallic Nanostructure", T. Shoji, et al., Y. Tsuboi, *J. Phys. Chem. C*, **2013**, *117(6)*, 2500.
3. "Resonant Excitation Effect on Optical Trapping of Myoglobin: The Important Role of a Heme Cofactor" T. Shoji, et al. Y. Tsuboi, *J. Phys. Chem. C*, **2013**, *117(20)*, 10691.
4. "Permanent Fixing or Reversible Trapping and Release of DNA Micropatterns on a Gold Nanostructure Using Continuous-Wave or Femtosecond-Pulsed Near-Infrared Laser Light", T. Shoji, et al., Y. Tsuboi, *J. Am. Chem. Soc.*, **2013**, *135(7)*, 6643.
5. "Plasmonic Optical Tweezers toward Molecular Manipulation: Tailoring Plasmonic Nanostructure, Light Source, and Resonant Trapping", T. Shoji, et al., Y. Tsuboi, *J. Phys. Chem. Lett.*, **2014**, *5*, 2957. (*Highlighted as ACS Editor's Choice*)
6. "Plasmonic optical tweezers: A long arm and a tight grip", Y. Tsuboi, *Nat. Nanotech.* **2016**, *11*, 5.
7. "Highly Sensitive Detection of Organic Molecules on the Basis of a Poly(*N*-isopropylacrylamide) Microassembly Formed by Plasmonic Optical Trapping", T. Shoji, et al., Y. Tsuboi, *Anal. Chem.*, **2017**, *89*, 532.

Plasmonic Optical Tweezer toward Molecular Manipulation

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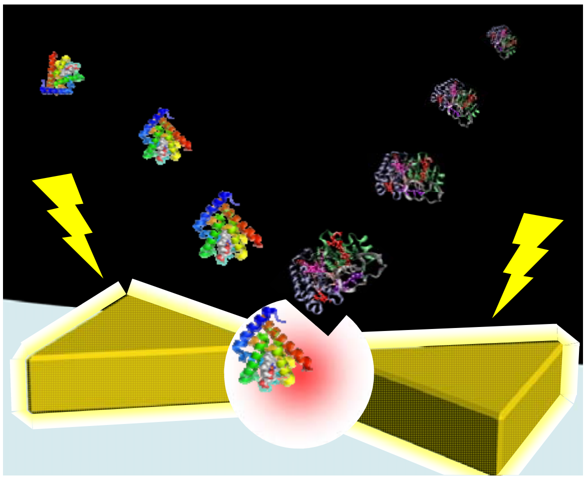
Plasmonic enhanced electromagnetic field is applicable not only to SERS but also to chemical reaction promotion, and also even to optical trapping. Plasmon-based optical trapping is quite intriguing and is currently attracting much attention in nano-photonics and related research fields, since optical trapping based on surface plasmon can potentially overcome several disadvantages of conventional optical trapping technique using a focused laser beam, i.e.; (i) the conventional technique requires an intense focused laser light and a complicated optical set up to manipulate a small nanoparticle, and (ii) the spatial resolution in the trapping is, as a matter of course, regulated to be more than several hundred nanometers by a diffraction limit of an incident light. As has been predicted theoretically and verified experimentally, an electromagnetic field of incident light should be considerably localized and enhanced at a nano-junction or a nano-gap between metal nanoparticles, so called gap-mode excitation. A schematic illustration for such plasmon-based optical trapping is displayed in the figure.



When photochemically-active species is trapped at such a plasmonic nan-gap, photon, plasmon, and the photoactive species should be simultaneously coupled in the same nano-space. We consider that such situation is an ideal photochemical reaction field in which they interact with each other with great efficiency to promote photochemical reaction yield. The goal of our study is to incarnate such situation. We have developed a plasmonic optical tweezer system and succeeded in novel trapping so far.

References

1. ‘Plasmonic optical trapping for artificial polymer system’, *J. Phys. Chem. C*, **2012** .
2. ‘Resonant optical trapping for polymer microsphere and a protein’ *J. Phys. Chem. C*, **2013**.
3. ‘Micro-pattern formation (colloidal crystal formation) on a plasmonic nanostructure’, *J. Phys. Chem. C*, **2013**.
4. ‘Quantitative evaluation for radiation pressure and Soret force (temperature elevation at a plasmonic nanostructure)’, *J. Phys. Chem. C*, **2012**.
5. ‘Femtosecond plasmonic optical tweezer for biomolecules (DNA)’, *J. Am. Chem. Soc.*, **2013**.

Recent advances of our researches are summarized in *J. Phys. Chem. Lett.*, **2014** and partly in *Nature Nanotechnology*, **2016**. The plasmonic optical tweezers can be applied also to analytical chemistry (*Anal. Chem.*, **2017**). Characteristics and strategy of our plasmonic optical tweezers are introduced toward molecular trapping.

8th RSC-CSJ Joint Symposium 2017
－Recent Developments in Plasmonics－

■Date　March 18th (Sat), 2017　9:00-17:20

■Venue　S3; Room J29,　House B, Bldg. 4,
Hiyoshi Campus, Keio University
Yokohama, Kanagawa, Japan

■Hosted by
The Chemical Society of Japan (CSJ)
Co-hosted by The Royal Society of Chemistry (RSC)

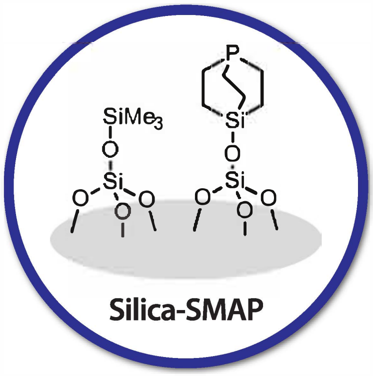
Publication: March 2017
Publisher: The Chemical Society of Japan
1-5, Kanda-Surugadai, Chiyoda-ku Tokyo, 101-8307, Japan

Silica-SMAP

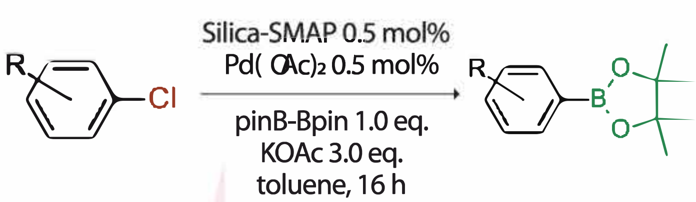
Cage-type Monophosphine Ligand

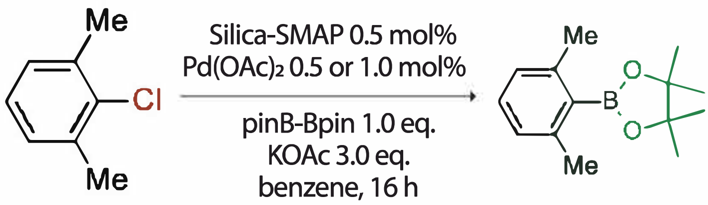
Features

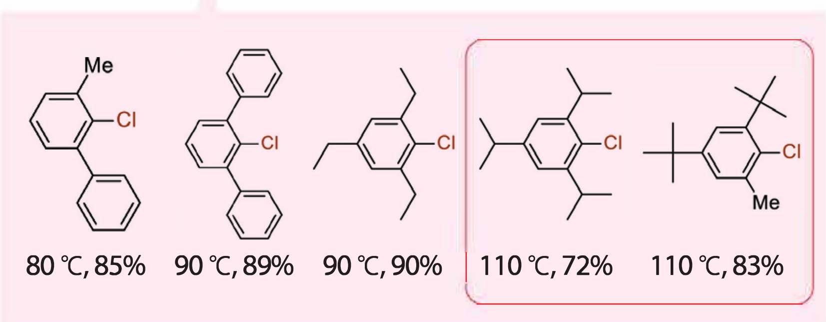
① Suzuki-Coupling of Ar-Cl substrates
② Borylation of bulky Ar-Cl substrates
③ Regioselective C-H borylation
④ Caged phoshines allow catalysts to be stable in the air.
⑤ Palladium is separated from the products by Celite filtration. [1]



Reactions [2),3)]







Borylation of bulky Ar-Cl substrates

Entry	Ligand	[Pd]/[L]	NMR Yield (%)
1	Silica-SMAP	1:1	93
2	SPhos	1:1	0
3	SPhos	1:2	0
4	XPhos	1:1	0
5	XPhos	1:2	0

Depending Silica-SMAP is a highly on the substrate, active than Buchwald Ligand.

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Product List

Product No.	Product Name	Grade	Package size
197-17451	Silica-SMAP	Organic Synthesis	1g
193-17453	Silica-SMAP	Organic Synthesis	5g

Wako Pure Chemical Industries, Ltd.

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