RESEARCH ACTIVITIES

Center for Mesoscopic Sciences

In the past few decades, great progress in experimental and theoretical methods to analyze structures, dynamics, and properties of single-component (or single hierarchical) molecules and nanomaterials has been made. Now we should also direct our attention to properties and functions of multi-hierarchical molecular systems. We develop innovative methods of measurements and analysis for molecular and materials systems to elucidate the processes that trigger the functions and reactions of the systems in the mesoscopic regime, that is the regime where micro and macroscopic properties influence each other.

Nano-Optical Imaging and Application to Nanomaterials

Center for Mesoscopic Sciences
Division of Supersensitive Measurements

OKAMOTO, Hiromi
Professor
[aho@ims.ac.jp]

Education
1983 B.S. The University of Tokyo
1991 Ph.D. The University of Tokyo

Professional Employment
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
Professor, The Graduate University for Advanced Studies

Award
2012 The Chemical Society of Japan (CSJ) Award for Creative Work

Member
Assistant Professor
NARUSHIMA, Tetsuya
YOSHIZAWA, Daichi
Project Assistant Professor (NINS)
AHN, Hyo-Yong
Post-Doctoral Fellow
HASHIYADA, Shun
YMANISHI, Junsuke
Visiting Scientist
WU, Yi-Ju*
Technical Fellow
ISHIKAWA, Akiko
Secretary
NOMURA, Emiko

Keywords Nano Optics, Plasmons, Chirality

Studies of local optical properties of molecular assemblies and materials are key to understanding nanoscale physical and chemical phenomena, and for construction of nanoscale functional devices. Nano-optical methods, such as scanning near-field optical microscopy (SNOM), enable optical imaging with spatial resolution beyond the diffraction limit of light. Combination of nano-optical techniques with various advanced spectroscopic methods may provide a methodology to analyze nanoscale functionalities and dynamics directly. It may yield essential and basic knowledge to understand origins of characteristic features of the nanomaterial systems. We have constructed nano-optical (near-field and far-field) spectroscopic and microscopic measuring systems, for the studies on excited-state properties of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable nano-optical measurements of two-photon induced emission, femtosecond time-resolved signals, and chiro-optical properties (as typified by circular dichroism), in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatial and temporal behavior of various metal-nanostructure systems and molecular assemblies. Typical examples are shown in Figure 1. We succeeded in visualizing wave functions of resonant plasmon modes in single noble metal nanoparticles, confined optical fields in noble metal nanoparticle assemblies. In recent few years, we have succeeded in observing plasmon wave packet propagation dynamics with ultrafast time-resolved near-field imaging, local chiro-optical properties of chiral and achiral metal nanostructures, and so forth. We also developed far-field high-precision circular dichroism microscope that facilitate chirality analysis of materials in a wide range of research areas. The information on nano-optical properties of the materials are also relevant to exploration of novel optical manipulation principles, which is another research topic of the research group.

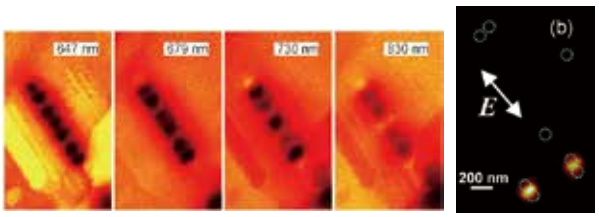


Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spheric gold nanoparticles (diameter 100 nm) observed at 785 nm. The arrows indicates the incident light polarization. Dotted circles represent approximate positions of the particles.

Selected Publications

- H. Okamoto, T. Narushima, Y. Nishiyama and K. Imura, "Local Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging," *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).
- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).
- H. Okamoto and K. Imura, "Near-Field Optical Imaging of Enhanced Electric Fields and Plasmon Waves in Metal Nanostructures," *Prog. Surf. Sci.* **84**, 199–229 (2009).

1. Active Control of Chiral Optical Near-Fields on a Single Metal Nanorod[1)]

Chiral optical fields (typified by circularly polarized light) localized on the nanoscale enhance the chiral light–matter interaction, which may provide novel potential applications. This property enables the development of an ultrasensitive method for characterization of chiral molecules and nanoscale magnetic control realized by an all-optical method to interconnect spintronic nano-optical devices. A local chiral light source with switchable handedness or controllable chirality is indispensable for building such applications for practical use. In the current major method used for local chiral light generation, the handedness of the light is controlled by the handedness of the nanomaterial, which is not convenient when we need to change the handedness of the light. We experimentally achieve here generation and active control of a highly chiral local optical field by using a combination of an achiral gold nanorod and achiral linearly polarized optical field. By tilting the azimuth angle for the incident linear polarization relative to the axis of the nanorod, either left- or right-handed circularly polarized local optical fields can be generated. Our work may give us a chance to pioneer analytical applications of chiral optical fields and novel spintronic nano-optical devices.

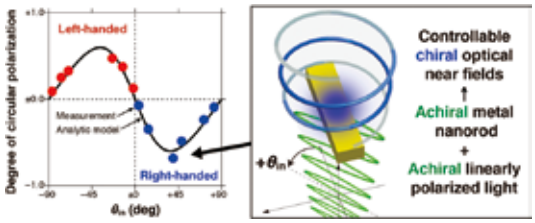


Figure 2. Right: Scheme of optical arrangement. A gold nanorod is illuminated by linearly polarized light with the E-field direction rotated for θ_m from the rod axis. Left: Experimentally obtained degree of circular polarization near the rod vs. polarization angle θ_m.[1)]

2. Circularly Polarized Photoluminescence from Achiral Dye Molecules Induced by Plasmonic Two-Dimensional Chiral Nanostructures[2)]

Strong dissymmetry between left- and right-handed circularly polarized photoluminescence (PL) enhancement induced by 2-dimensional chiral gold nanostructures was found, which can be utilized to provide a circularly polarized luminescence source. Lightning-bolt-like (composed of two displaced rectangles) chiral plasmonic gold nanostructures were fabricated on a glass substrate and were adopted as materials to induce dissymmetry in PL enhancement. We employed achiral IR125 dye as an achiral molecular PL emitter with luminescence that was enhanced by near-field interaction between the chiral plasmon and the molecule. PL decay measurements confirmed that the PL enhancement arose from the plasmonic effect. Large PL enhancement dissymmetry factors $g \sim 0.14$ were obtained in the wavelength region near 800 nm. The dissymmetry of PL enhancement showed maximum amplitudes at 800–850 nm, which approximately correspond to the wavelength providing maximal extinction dissymmetry (~800 nm) of the lightning-bolt-like structure, and is resonant with a chiral multipolar plasmon mode. The dissymmetry was relatively small at the wavelength resonant with a dipolar plasmon mode.

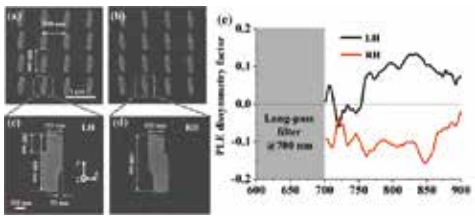


Figure 3. (a–d) Electron micrographs of chiral gold nanostructures. (e) Photoluminescence enhancement (PLE) dissymmetry spectra for luminescence from IR125 dye combined with left-handed (black) and right-handed (red) gold nanostructures.[2)]

3. Visualization of Enantiomeric Excess of Chiral Metal-Organic Framework Microparticles by Circular Dichroism Imaging[3)]

Circular dichroism (CD) microscopic images of microcrystalline particles of a microporous, robust, and chiral metal–organic framework (MOF) were observed to estimate enantiomer excess (ee) of the synthesized particles. La(btb) (btb = 1,3,5-tris(4-carboxylatephenyl)benzene), a thermally and chemically robust MOF, was employed in this study because it shows a chiral space group. Although La(btb) has been obtained as a racemic conglomerate, enantioselective synthesis of La(btb) was achieved via a chiral precursor complex consisting of lanthanum and homochiral phenylalanine. Methyl orange (MO) was introduced into the micropores of chiral La(btb), which showed a strong induced CD signal for the absorption band of MO chromophores. High ee of the synthesized chiral La(btb) was revealed by microscopic CD observation at the single particle-level. This result provides a facile way to obtain a robust MOF that has chiral nanospace, and demonstrates the potential utility of CD microscopy to define handedness of many microcrystalline particles at the same time.

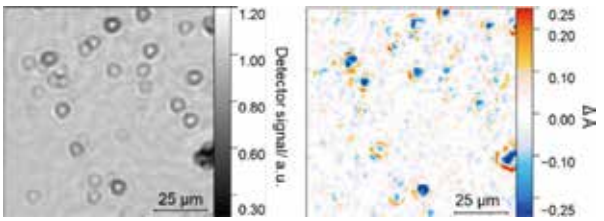


Figure 4. Transmission (left) and CD (right) microscopic images of $MO_{0.35}$@L-La(btb).[3)] Most of the particles showed the same CD signals.

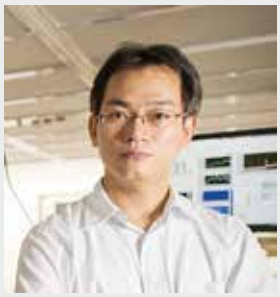
References

1) S. Hashiyada, T. Narushima and H. Okamoto, *ACS Photon.* **6**, 677–683 (2019).
2) K. Q. Le, S. Hashiyada, M. Kondo and H. Okamoto, *J. Phys. Chem. C* **122**, 24924–24932 (2018).
3) T. Yamada *et al.*, *Chem. –Eur. J.* **25**, 6698–6702 (2019).

* IMS International Internship Program (Graduate Student from National Chiao Tung University, Taiwan)

Ultrafast Laser Science

Center for Mesoscopic Sciences
Division of Broadband Multiscale Analysis



FUJI, Takao
Associate Professor
(–March, 2019)
[fuji@ims.ac.jp]

Education
1994 B.S. University of Tsukuba
1999 Ph.D. University of Tsukuba

Professional Employment
1999 Assistant Professor, The University of Tokyo
2002 JSPS Postdoctral Fellowship for Research Abroad, Vienna University of Technology (–2004)
2004 Guest Researcher, Max-Planck-Insitute of Quantum Optics
2006 Research Scientist, RIKEN
2008 Senior Scientist, RIKEN
2010 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2019 Professor, Toyota Technological Institute

Awards
1999 Encouragement Award, The Optical Society of Japan
2008 Kondo Award, Osaka University
2015 Laser Research Development Award, the Laser Society of Japan

Member
Assistant Professor
NOMURA, Yutaka
IMS Fellow
REZVANI, Seyed Ali
Visiting Scientist
HUANG, Wei-Hong
Graduate Student
KUMAKI, Fumitoshi
ITOH, Takuma*
Secretary
MASUDA, Michiko

Keywords Ultrafast Science, Laser Physics, Nonlinear Optics

Light is very common in daily life, on the other hand, light has many interesting physical properties, for example, constancy of velocity, wave-particle duality, *etc*. The study of light itself is still important in modern physics.

Light is electro-magnetic field, same as radio wave, however, the measurement of the waveform of light is not easy task even in the 21st century. The difficulty comes from the extremely fast oscillation of the light wave. The oscillation frequency of light wave is the order of hundred terahertz (THz = 10^{12} Hz), in other words, the oscillation period of light wave is the order of femtosecond (fs = 10^{-15} s).

In 2013, we have developed a new method for the measurement of light wave. It is called FROG-CEP, frequency-resolved optical gating capable of carrier-envelope determination. Our method does not need attosecond pulses, even self-referencing is possible. The electric field oscillations of infrared light with the period of several femtoseconds were clearly measured with the method as is shown in Figure 1.

Currently, amplitude modulation and phase modulation are common encoding techniques in optical communication. If we can encode information in the shape of the light wave itself, the communication speed becomes 3 orders of magnitude faster. We believe that our method, FROG-CEP, becomes very important to realize such communication technology.

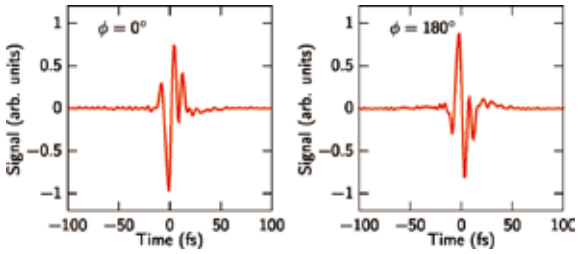


Figure 1. Infrared light waveforms measured with FROG-CEP. The phase difference between the two infrared pulses was clearly measured.

Other than FROG-CEP, ultrabroadband mid-infrared continuum generation through filamentation, single-shot detection of ultrabroadband mid-infrared spectra, and development of 2 μm ultrafast lasers have been realized in our laboratory. We are developing such cutting edge technologies for ultrafast laser science.

Selected Publications

- Y. Nomura, H. Shirai and T. Fuji, "Frequency-Resolved Optical Gating Capable of Carrier-Envelope Phase Determination," *Nat. Commun.* **4**, 2820 (11 pages) (2013).
- Y. Nomura M. Nishio, S. Kawato and T. Fuji, "Development of Ultrafast Laser Oscillators Based on Thulium-Doped ZBLAN Fibers," *IEEE J. Sel. Top. Quantum Electron.* **21**, 0900107 (7 pages) (2015).
- T. Fuji, Y. Nomura and H. Shirai, "Generation and Characterization of Phase-Stable Sub-Single-Cycle Pulses at 3000 cm^{-1}," *IEEE J. Sel. Top. Quantum Electron.* **21**, 8700612 (12 pages) (2015).
- H. Shirai, Y. Nomura and T. Fuji, "Self-Referenced Measurement of Light Waves," *Laser Photonics Rev.* **11**, 1600244 (6 pages) (2017).
- S. A. Rezvani, M. Suzuki, P. Malevich, C. Livache, J. V. de Montgolfier, Y. Nomura, N. Tsurumachi, A. Baltuska and T. Fuji, "Millijoule Femtosecond Pulses at 1937 nm from a Diode-Pumped Ring Cavity Tm:YAP Regenerative Amplifier," *Opt. Express* **26**, 29460–29470 (2018).

1. Development of Intense Femtosecond Lasers at 2 μm[1)]

Intense ultrashort infrared pulse lasers are highly attractive in many research fields. Powerful femtosecond pulses in the vicinity of 2 μm are desired for coherent mid-infrared or terahertz pulse generation, high harmonic generation in the water window soft x-ray region, and atmospheric sensing. In order to obtain intense femtosecond pulses around the 2 μm wavelength region, one of the most widely used schemes is optical parametric amplification (OPA) with well-established ultrafast pump lasers such as Ti:sapphire or Yb lasers. However, OPA in general has a complicated design due to the requirement of the precise synchronization between the pump and seed pulses. This fact attracts a lot of attention to the development of solid-state lasers which directly generate high energy ultrashort pulses around 2 μm.

In this work we present a new table-top Tm:YAP laser system based on a diode-pumped ring cavity regenerative amplifier. The system generates 360 fs pulses at 2 μm with the peak power of 2 GW after the compression.

The schematic of the system is shown in Figure 2. The seed source of the laser system is a Tm:ZBLAN fiber oscillator,[2)] which generates 2 μm pulses with the pulse energy of 4 nJ. The pulses are sent to a grating stretcher and then to a ZBLAN fiber pre-amplifier pumped by a laser diode at 794 nm.[3)]

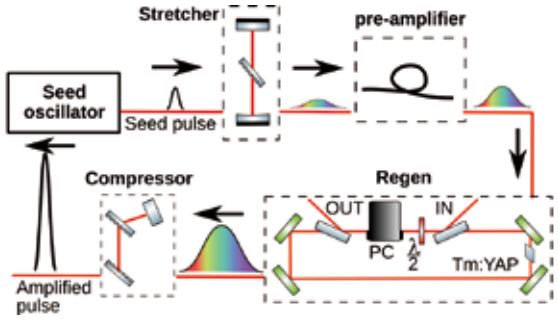


Figure 2. Schematic of the system. PC: Pockels cells.

The amplified seed pulses (~100 nJ) are picked with 1 kHz rate by a Pockel cell and are sent to a regenerative amplifier based on a Brewster-cut, 4% doped, 12 mm long Tm:YAP crystal which is pumped by another 794 nm laser diode. The output power of the regenerative amplifier is 1.4 W with the absorbed pump power is 23.5 W at 45 round trips. The output pulse is compressed using a pair of gratings. The energy of the compressed pulse is 0.924 mJ.

The compressed pulse was characterized using a home-built SHG-FROG system. The temporal and spectral profile of the pulse obtained by the system are shown in Figure 3. The pulse duration is 360 fs.

The compressed pulses exhibit good beam profile and can be directly used to generate white light in bulk materials. Using only 15 μJ of the amplified pulse, we have generated

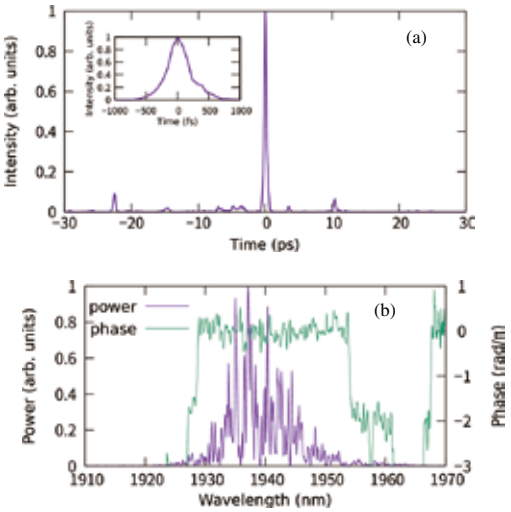


Figure 3. (a) Temporal profile of the pulse from the amplifier. Inset: Zoomed view of the main pulse peak. (b) Power spectrum and spectral phase of the pulse.

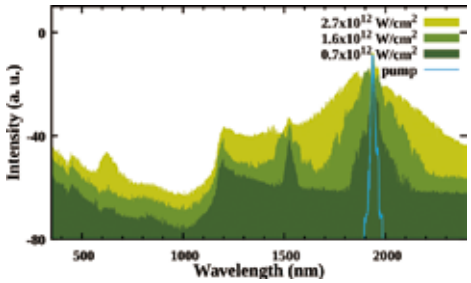


Figure 4. Variation of the generated white light with the changes of the pump intensity.

white light in a 3 mm YAG crystal. The white light spectra are shown in Figure 4.

Such properties combined with the good power scalability over a wide range of available pumping energies makes this scheme a viable candidate for direct application for mid-infrared OPA. In particular, the system exhibits a flexible electronic control on the obtainable output energy through changes in round trips, pumping energy, and repetition rate. The feature makes it a good candidate for many applications such as spectroscopy which would require a tight control over the light source. The proposed ring regenerative amplifier provides a versatile and simple infrared source that can be used in many of the current applications, in a compact table-top design.

References

1) S. A. Rezvani, M. Suzuki, P. Malevich, C. Livache, J. V. de Montgolfier, Y. Nomura, N. Tsurumachi, A. Baltuska and T. Fuji, *Opt. Express* **26**, 29460 (2018).

2) Y. Nomura, M. Nishio, S. Kawato and T. Fuji, *IEEE J. Sel. Top. Quantum Electron.* **21**, 0900107 (2015).

3) Y. Nomura and T. Fuji, *Appl. Phys. Express* **10**, 012703 (2016).

* carrying out graduate research on Cooperative Education Program of IMS with Kagawa University