5th Symposium on
“Applications of Light and Materials for the Innovation of Technology and Life”
13:15 to 16:15 on 18th March 2015
Auditorium of AIST Shikoku Center
2217-14 Hayashi-Cho, Takamatsu, Kagawa 761-0395, Japan

Program

Session I: 13:15~14:45
Chairman: Dr. Shin-ichi Wakida (AIST)

Invited Lecture 1: 13:15~13:45
Functional Hybrid Structures of Colloidal Nanocrystals
Prof. Andrey Rogach (City University of Hong Kong)

Invited Lecture 2: 13:45~14:15
Early Detection of Diseases by using Lipid Peroxidation Biomarkers
Dr. Yasukazu Yoshida (AIST)

Invited Lecture 3: 14:15~14:45
Femtosecond Four-Wave Mixing Spectroscopy and its Application to Nano-Photonics and Molecular Vibrational Dynamics
Prof. Shunsuke Nakanishi (Kagawa University)

Session II: 14:45~16:15
Chairman: Prof. Masahiro Funahashi (Kagawa University)

Invited Lecture 4: 14:45~15:15
Plasmon-Induced Artificial Photosynthesis Systems
Prof. Hiroaki Misawa (Hokkaido University)

Invited Lecture 5: 15:15~15:45
A Multicolor Luciferase Assay System for Monitoring Multiple Gene Expressions
Dr. Mayu Yasunaga (AIST)

Invited Lecture 6: 15:45~16:15
Control of Multiexciton Dynamics in a Single Colloidal Quantum Dot by Localized Surface Plasmon
Prof. Sadahiro Masuo (Kwansei Gakuin University)

16:15~17:00 - Refreshment
Functional Hybrid Structures of Colloidal Nanocrystals

Andrey L. Rogach

Prof. Rogach is a Chair Professor of Photonics Materials at the Department of Physics and Materials Science and the Founding Director of the Centre for Functional Photonics at City University of Hong Kong, an Associate Editor of ACS Nano, and honorary professor at Trinity College Dublin

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Keywords: Metal nanoparticles, Semiconductor quantum dots, Nanowire, Nanocrystal assembly

Abstract: Colloidal semiconductor and metal nanocrystals of different sizes, shapes and compositions can nowadays be synthesized in large quantities by inexpensive and versatile solution based approaches. They are attractive for use as building blocks in different functional nanostructures. We provide an overview of colloidal nanoparticles synthesized in our labs and demonstrate several approaches for nanocrystal’s assembly. Advanced optical spectroscopy provides important insights into fundamental photophysical properties of these nanostructures, such as the energy and charge transfer. Different related application aspects ranging from light-emitting diodes and water-splitting materials to biological markers will be discussed.

Invited Lecture 2
13:45~14:15

Early Detection of Diseases by using Lipid Peroxidation Biomarkers

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Keywords: Lipid peroxidation, Oxidative stress, HODE, Oxycholesterol, HETE

Abstract: We developed a novel method to measure hydroxyoctadecadienoic acid (HODE) levels in biological fluid and tissue samples. This method can be used to measure a considerable amount of the oxidation products of linoleic acid. Reduction and saponification enabled us to measure hydroperoxides and hydroxides of both free and esterified forms of linoleic acid as total HODE, which includes the enzymatic and non-enzymatic product 9,13-(Z, E)-HODE; the non-enzymatic free radical-mediated product 9,13-(E, E)-HODE; and the specific non-enzymatic singlet oxygen-mediated product 10,12-(Z, E)-HODE. We have recently reported HODE levels in plasma and
erythrocytes in healthy volunteers and patients with diabetes, nonalcoholic steatohepatitis, nephritis, Alzheimer’s diseases, and Parkinson’s disease, among other diseases and determined that its levels are much higher in patients with lifestyle-related diseases than in healthy volunteers. Furthermore, the plasma levels of 10- and 12-\((Z, E)\)-HODE, which are singlet oxygen-specific products, can serve as promising biomarkers for the early detection of diabetes. Thus, HODE is a useful biomarker for the assessment of oxidative status, and it may be strengthened by using it in combination with other typical biomarkers. This review article focused on lipid peroxidation biomarkers, including HODE and discusses their potential practical and clinical applications in disease prediction.

**Invited Lecture 3**
14:15~14:45

**Femtosecond Four-wave mixing spectroscopy and its application to nano-photonics and molecular vibrational dynamics**

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**Keywords:** Four-wave mixing spectroscopy, Optical dephasing, Quantum dots, Molecular vibration

**Abstract:** We present the principle and potentials of femtosecond four-wave mixing (FWM) spectroscopy and its applications to the unveiling of optical dephasing of excitons in CdSe/ZnS quantum dots (QDs) and the ultrafast dynamics of coherent molecular vibrations in polymers.

FWM spectroscopy is a well-established technique for analyzing the nonlinear optical properties. In general, the FWM signals are generated from the nonlinear polarizations induced in the sample by three excitation light beams. It involves the so-called photon echoes phenomena and coherent anti-Stokes Raman spectroscopy (CARS). The FWM spectroscopy can detect much more detailed optical properties than the absorption and photoluminescence (PL) spectroscopy do, since the FWM signals reflect on the quantum phase coherence in the superposition states created by the three excitation beams. We have been interested in ultrafast optical dynamics of materials measured in the FWM spectroscopy by means of femtosecond laser pulses. We present the fundamental principle and experimental results of FWM spectroscopy applied to the optical dephasing of excitons in CdSe/ZnS QDs and molecular vibrations in polymers.

When QD solutions are excited by two femtosecond laser beams, as shown in Figure 1(a), with the same frequency in the absorption band of excitons, the
Fig. 1 Excitation geometry of FWM signals. (a) Two beam excitation and (b) three beam excitation.

degenerate FWM signals are emitted in the direction of $2k_2-k_1$. Figure 2(a) displays the time profiles of FWM signals, with respect to the time delay $\tau$ between the two pulses, measured for QDs in two solvents [1]. The decays of these signals correspond to the relaxations of quantum phase coherence between the excited and ground exciton states; in other words, coherent polarizations are inversely proportional to the homogeneous line widths of exciton transitions. It is clearly observed that the decay of FWM signals in cyclohexane is much slower than that in benzene, which indicates that the interaction of QDs with benzene molecules gives rise to much faster phase relaxation of excitons. This kind of change in the optical properties cannot be detected by using conventional absorption and PL spectroscopy.

Fig. 2 (a) FWM signals measured for CdSe/ZnS QDs in cyclohexane and benzene solutions, and (b) CARS signal measured for CH$_2$ stretching modes in polyethylene at 2900 cm$^{-1}$ and 6 K.

If we excite the sample by three femtosecond laser pulses as shown in Figure 1(b), the sample emits the FWM signal in the direction of $k_s=k_1+k_3-k_2$ only when the frequency difference ($\omega_1-\omega_2$) between the two pulses is tuned to be a specific molecular vibration. In this case, the FWM signals are called as the CARS signals and originate from the induced coherent vibrational state in the sample. Figure 2(b) represents one of the CARS signals observed at 2850 cm$^{-1}$ for CH$_2$ stretching vibration modes in polyethylene at 6 K [2]. The signals consists of fast ($T_2=90$ fs) and slow ($T_2=450$ fs) decays, which correspond to the anti-symmetric and symmetric vibration modes, respectively.

Invited lecture 4:
14:45~15:15

Plasmon-Induced Artificial Photosynthesis Systems

Hiroaki Misawa

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Keywords: Surface plasmon, Solar water splitting, Artificial photosynthesis

Abstract: We have demonstrated plasmonic photocurrent generation from visible to near-infrared wavelengths without deteriorating photoelectric conversion using electrodes in which gold nanorods are elaborately arrayed on the surface of a TiO$_2$ single crystal.$^{1-3}$ We have also reported the stoichiometric evolution of oxygen via water oxidation by irradiating the plasmon-enhanced photocurrent generation system with near-infrared light.$^{4-6}$ In the present study, we developed a plasmon-assisted water splitting system that operates under irradiation by visible light; the system is based on the use of two sides of the same strontium titanate (SrTiO$_3$) single crystal substrate.$^7$ The water splitting system contains two solution chambers to separate hydrogen (H$_2$) and oxygen (O$_2$), respectively. To promote water splitting, a chemical bias was applied by pH values regulations of those chambers. The quantity of H$_2$ evolved from the surface of platinum, which was used as a reduction co-catalyst, was twice of O$_2$ evolved from an Au nanostructured surface. Thus, the stoichiometric evolution of H$_2$ and O$_2$ was clearly demonstrated. The hydrogen evolution action spectrum closely corresponds to the localized surface plasmon resonance spectrum, indicating that the plasmon-assisted charge separation at the Au/SrTiO$_3$ interface promotes water oxidation and the subsequent reduction of a proton on the backside of the SrTiO$_3$ substrate. We have elucidated furthermore that the chemical bias is dramatically reduced by plasmonic effects, which indicate the possibility of constructing an artificial photosynthesis system with low energy consumption.

According to the analogous method of the water splitting system, we have successfully constructed the artificial-photosynthesis system which produces the ammonia by a photofixation of a nitrogen molecule based on visible light irradiation.$^8$ Unlike the water splitting system, ruthenium is used as a co-catalyst instead of a platinum for the ammonia synthesis, and not a solution system but a gas system is used to reduce nitrogen gas. The action spectrum of the apparent quantum efficiency of ammonia evolution showed good agreement with the plasmon resonance spectrum. Therefore, we succeeded in photoelectrochemical synthesis of ammonia by the visible light irradiation through the plasmon-induced charge separation.
A multicolor luciferase assay system for monitoring multiple gene expressions.

Mayu Yasunaga and Yoshihiro Nakajima

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**Keywords:** Bioluminescence, Luciferase, Gene expression, Bioimaging

**Abstract:** Bioluminescent reporters, which emit light by oxidizing its substrate luciferin, have become an essential tool for studying various aspects of biological functions, including gene expression, posttranscriptional modification and protein–protein interactions, because the sensitivity and range of the linear response are superior to those of other reporters, including β-galactosidase, chloramphenicol acetyltransferase, and fluorescent proteins. In particular, luciferases are used as sensitive probes to monitor gene expression, quantitatively, and longitudinally in living cells, explant tissues, and in vivo.

Fluorescent proteins have contributed immensely to the advancement of cell biology and are used as powerful probes to monitor an extensive array of entities, ranging from single molecules to whole organisms. However, fluorescent reporters require exogenous illumination to emit light, making them unsuitable for the long-term quantitative monitoring of gene expression because the reporter is bleached and the subject can suffer phototoxic damage caused by repetitive exogenous illumination.

Recent advances in luciferase technology, involving improvements in both the luciferase and the detection system and a newly cloned luciferase gene, allow us to monitor the expression of multiple genes simultaneously when luciferase are used that
induce differently colored emission spectra in the catalysis of a common substrate. Recently, we have developed a multicolor luciferase assay system in which multiple gene expressions can be simultaneously monitored using green-, orange- and red-emitting beetle luciferases. Using this system, we have successfully monitored multiple gene expressions simultaneously, such as clock genes, inflammatory cytokine genes in vitro and ex vivo, and applied to cell based assay. In this seminar, I would like to present and discuss basic, utility and possibility of the luciferase assay system for life science study, drug discovery and chemical risk analysis.

Invited lecture 6:
15:45~16:15

Control of Multiexciton Dynamics in a Single Colloidal Quantum Dot by Localized Surface Plasmon

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Keywords: Quantum dots, Multiple exciton generation, Auger recombination, Photon antibunching

Abstract: One of the important exciton dynamics of semiconductor quantum dots (QD) is simultaneous existence of multiple excitons (MX) in a single QD. By utilizing the MX, the efficiency of the optoelectronic devices can be considerably increased. However, when MX generates in a single QD, exciton annihilation process which is called the Auger recombination occurs. To utilize the MX, the Auger recombination has to be suppressed. On the other hand, if the Auger recombination efficiently occurs, a single QD can be used as a single-photon source which is an important for the quantum information technology. Therefore, it is important to control the MX dynamics. Previously, we investigated photon antibunching behavior of a single QD interacted with metal nanostructures. As results, we revealed that the Auger recombination process could be suppressed by the interaction with the metal nanostructure.[1-3] To reveal the mechanism of the exciton dynamics in more detail, the best way is the direct observation of the emission behavior with the coupling of a single QD with a single metal nanostructure with well-defined size and shape. In this work, AFM manipulation technique was employed to couple a single QD with a metal nanostructure, i.e., a single gold nanocube (AuCube) was approached to a single CdSe/ZnS QD using the AFM manipulation.

Figure 1 shows AFM images (a, c) and fluorescence images (b, d) observed simultaneously from a same area before (a, b) and after (c, d) the AFM manipulation of an AuCube. In Fig. 1(a), the AuCube marked by a square was pushed to a single
Fig. 1 AFM images (a, c) and fluorescence images (b, d) before (a, b) and after (c, d) AFM manipulation of an AuCube. A square and circles in the images indicate AuCube and QD, respectively.

QD marked by a circle. After the manipulation, the distance between the AuCube and the QD was shortened to 5 nm (center-to-center distance). In the fluorescence images, a slight change of the fluorescence intensity was observed. To understand the emission behavior, the time traces of the fluorescence intensity, fluorescence decay curves, fluorescence spectra, and photon antibunching of the single QD were measured before and after the manipulation. As results, the increase in the fluorescence intensity, the shortening of the decay curve, and the decrease in the probability of photon antibunching were observed after the manipulation. Furthermore, the modified emission behavior was changed to original emission behavior by separating the AuCube from the QD. These results clearly indicated the exciton dynamics can be controlled by the coupling of AuCube with the single QD, i.e., the Auger recombination can be suppressed by the interaction with AuCube. We will discuss the mechanism in more detail.