Nano-Optical Imaging and Application to Nanomaterials

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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.

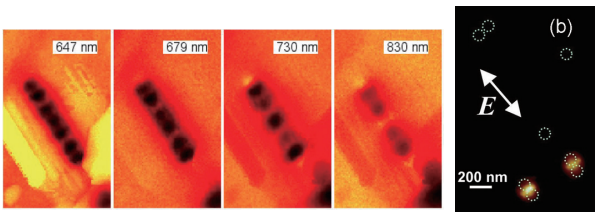

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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, "Local Optical Activity of Nano- to Microscale Materials and Plasmons," *J. Mater. Chem. C* **7**, 14771–14787 (2019).
- 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).

1. Roles of Superchirality and Interference in Chiral Plasmonic Biodetection[1)]

Chiral plasmonic nanostructures enable ≤pg detection and characterization of biomaterials. The sensing capabilities are associated with the chiral asymmetry of the near fields, which locally can be greater than equivalent circularly polarized light, a property referred to as superchirality. However, sensing abilities do not simply scale with the magnitude of superchirality. We show that chiral molecular sensing is correlated to the thickness of a nanostructure. This observation is reconciled with a previously unconsidered interference mechanism for the sensing phenomenon. It involves the "dissipation" of optical chirality into chiral material currents through the interference of fields generated by two spatially separated chiral modes. The presence of a chiral dielectric causes an asymmetric change in the phase difference, resulting in asymmetric changes to chiroptical properties. Thus, designing a chiral plasmonic sensor requires engineering a substrate that can sustain both superchiral fields and an interference effect.

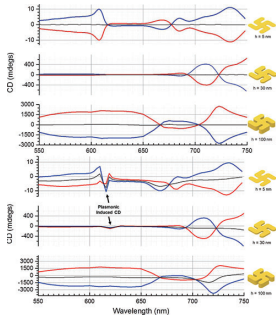

Figure 2. Simulated CD spectra for gammadions of h = 5 nm, 30 nm, and 100 nm when light is incident upon their top (blue) and bottom (red) faces. Top three: Encapsulated by an achiral layer. Their mean is shown in black and is ~0 in all cases. Bottom three: Encapsulated by a chiral layer. The mean of the two incidences is shown in black.

2. Spectral Properties of Chiral Electromagnetic Near Fields Created by Chiral Plasmonic Nanostructures[2)]

The surface-enhanced chiral-optical spectroscopy is based on the interaction of chiral molecules with chiral electromagnetic near field localized on a chiral plasmonic nanostructure. It is of fundamental importance to reveal the spectral characteristics of chiral near fields for maximizing the chiral interaction. We investigated relations between near field and far field polarization characteristics of the chiral plasmonic nanostructures, using electromagnetic simulations. We found that spectral features of chiral near fields created by the nanostructures intercorrelate with those of far field optical rotation. This finding may provide us a method to characterize and design the chiral near field.

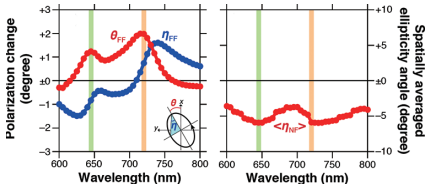

Figure 3. Simulated far-field circular dichroism η_{FF} (blue) and optical rotation θ_{FF} (red) spectra (top) and near-field circular dichroism η_{NF} spectrum (bottom) of a gold gammadion-shaped nanostructure (width 450 nm) by the finite-difference time-domain method.

3. Circularly Polarized Two-Photon-Induced Luminescence from Plasmonic Two-Dimensional Chiral Au Nanostructures[3)]

A chiral nanostructure, which exhibits optical activity, absorbs different amounts of left-handed circularly polarized (LCP) and right-handed circularly polarized (RCP) light. In this work, we report the observation of dissymmetry between two-photon-induced LCP and RCP photoluminescence from plasmonic two-dimensional (2D) chiral Au nanostructures. Under excitation by linearly polarized femtosecond pulses from a mode-locked Ti:sapphire laser with a low incident power of 3 mW, the 2D chiral plasmonic nanostructure yields circularly polarized two-photon-induced photoluminescence (TPIPL) due to resonance with a chiral multipolar plasmon mode of the nanostructure. The handedness of the circularly polarized TPIPL was dependent on the handedness of the chiral plasmonic nanostructure. The chiral nature of TPIPL may find potential applications in optical devices, sensing of chiral molecular environments in biological systems, and so forth.

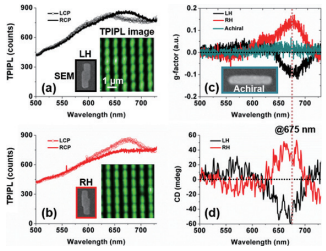

Figure 4. (a,b) Left- and right-circularly polarized TPIPL spectra of the chiral nanostructures. Insets: SEM and TPIPL microscopic images of the left- (a) and right-handed (b) chiral gold nanostructures. (c) Dissymmetry factor (g) spectra of TPIPL for the chiral and achiral nanostructures. (d) CD spectra of the chiral nanostructures.

References

1) C. Gilroy, S. Hashiyada, K. Endo, A. S. Karimullah, L. D. Barron, H. Okamoto, Y. Togawa and M. Kadodwala, *J. Phys. Chem. C* **123**, 15195–15203 (2019).
2) S. Hashiyada, K. Endo, T. Narushima, Y. Togawa and H. Okamoto, *J. Phys.: Conf. Ser.* **1220**, 012050 (2019).
3) K. Q. Le and H. Okamoto, *J. Phys.: Conf. Ser.* **1220**, 012004 (2019).

Award

OKAMOTO, Hiromi; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology Awards for Science and Technology Research Category (2020).

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