Nano-Optical Imaging and Application to Nanomaterials

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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.

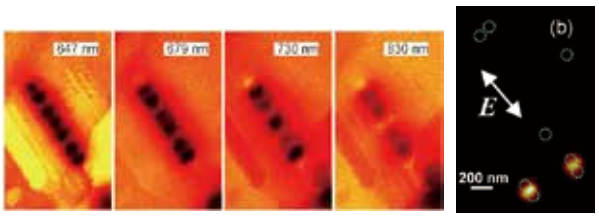

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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.

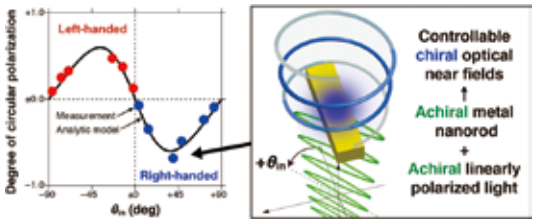

Figure 2. Right: Scheme of optical arrangement. A gold nanorod is illuminated by linearly polarized light with the E-field direction rotated for θ_m from the rod axis. Left: Experimentally obtained degree of circular polarization near the rod vs. polarization angle θ_m.[1)]

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.

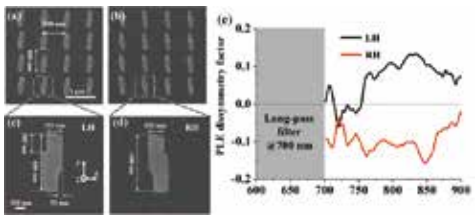

Figure 3. (a–d) Electron micrographs of chiral gold nanostructures. (e) Photoluminescence enhancement (PLE) dissymmetry spectra for luminescence from IR125 dye combined with left-handed (black) and right-handed (red) gold nanostructures.[2)]

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.

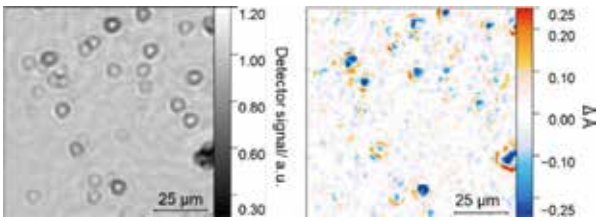

Figure 4. Transmission (left) and CD (right) microscopic images of $MO_{0.35}$@L-La(btb).[3)] Most of the particles showed the same CD signals.

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).

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