学 位 論 文 内 容 の 要 旨/Dissertation Abstract

博士（環境科学）　　氏　名/WANG Tianci

学 位 論 文 題 名/Title of Dissertation

Investigation of exciton-plasmon coupling in luminescent semiconductor quantum dot-gold nanoparticle systems

（発光半導体量子ドット−金ナノ粒子系における励起子−プラズモン結合の研究）

Semiconductor quantum dots (QDs) are nanoscale crystalline materials with unique size-dependent optical and electronic properties, making them highly promising for next-generation photonic and electronic devices. Due to quantum confinement effects, QDs exhibit tunable bandgaps, allowing precise control over their emission wavelengths by simply varying size or composition. They also demonstrate high photoluminescence quantum yields (PLQYs), broad absorption with narrow emission bands, and strong light absorption capabilities, which are advantageous for applications in solar cells, LEDs, lasers, photodetectors, and bioimaging. Initially, metal chalcogenide QDs such as CdSe, PbS, and CdTe dominated the field, offering high performance but raising environmental and health concerns due to their toxicity. In recent years, metal halide perovskite QDs, such as $CsPbX_3$, $MAPbX_3$ and $FAPbX_3$ (X = Cl, Br, I, and MA and FA are methylammonium and formamidinium cations, respectively), have gained attention for their excellent optoelectronic properties, defect tolerance, and straightforward synthesis from cost-effective precursors. These perovskite QDs have shown exceptional potential in light-harvesting and light-emitting applications. Overall, QDs are at the forefront of nanomaterials research, combining fundamental insights in photophysics with exciting opportunities for innovative device technologies. However, long-term stability, heavy metal toxicity, and multichannel excitonic recombination are some challenges, prompting efforts toward surface passivation, nontoxic alternatives, and exciton recombination control.

Exciton–plasmon coupling has emerged as a powerful strategy to modulate excitonic processes and enhance the light absorption efficiency of QDs. Localized surface plasmon resonance (LSPR), originating from the collective oscillation of free electrons in metal nanoparticles or nanostructures, can strongly interact with the dipole moments or photon fields of organic chromophores and QDs. This interaction leads to the formation of hybridized exciton–plasmon states, resulting in improved optical properties such as enhanced absorption and emission. LSPR can influence exciton behavior through various mechanisms, including near-field coupling, energy transfer, electron transfer, and far-field scattering. In particular, placing QDs within plasmonic cavities significantly strengthens exciton–plasmon coupling due to intense electromagnetic field confinement. Despite substantial progress, the detailed dynamics and efficiency of exciton–plasmon interactions remain incompletely understood, especially at the single-particle level. Most existing studies have been conducted on QD ensembles, overlooking important dynamic information revealed by

photoluminescence (PL) blinking in single QDs. This thesis aims to investigate the exciton–plasmon coupling mechanisms in metal chalcogenide and halide perovskite QDs, using both ensemble-level studies in plasmonic cavities and single-particle PL blinking analysis on plasmonic nanoparticles, to gain deeper insight into the coupling dynamics and optimize their performance for photonic applications.

C**hapter 1** introduces the general properties of semiconductor QDs with examples of metal chalcogenide QDs and metal halide perovskite QDs. Next, it presents the LSPR theory and exciton-plasmon coupling mechanisms in the weak and strong coupling frames, which is followed by introducing examples of plasmon enhanced ensemble PL and single QDs blinking without and with LSPR coupling. The final part of the chapter focuses on examples of exciton-plasmon coupling applied to LEDs, low threshold lasers, photocatalysis and photovoltaics.

C**hapter 2** forms the main materials and methods section of the thesis, providing complete details of chemicals, solvents, samples, and scientific instruments and software involved in understanding the PL and SPR of QD and Au nanoparticle systems. $MAPbI_3$ ligand-free QDs (BQDs) and ligand-capped QDs (LQDs) were synthesized by a modified spray method and a ligand-assisted reprecipitation method. Au nanorods (NRs) and CdSe-ZnS core-shell QDs (QD655 and QD624) were commercially obtained. This chapter also includes details of plasmonic substrate preparation and QD embedded plasmon cavity fabrication. Materials characterization methods such as transmission electron microscopy and high-resolution scanning transmission electron microscopy are included in this chapter.

C**hapter 3** is dedicated to understanding exciton-plasmon coupling in $MAPbI_3$ QD-Au NR systems. Both $MAPbI_3$ BQDs and LQDs illustrate slow ON-OFF blinking on SiO_2, which became more frequent short-living burst blinking on Au NRs, with 3-13 folds PL intensity enhancement. Based on single-particle PL blinking ON-OFF probability analyses, PL lifetime values, and ground-state bleaching-recovery kinetics for QD only and QD-Au NR samples, mechanisms on plasmon near field coupling and plasmon resonance energy transfer are discussed to account for enhanced PL intensity with suppressed ON time.

C**hapter 4** exclusively focuses on exciton-plasmon coupling in CdSe-ZnS QDs on Au NRs by analyzing the PL blinking dynamics and lifetimes of the QDs. Pristine CdSe-ZnS QDs exhibit frequent ON-OFF blinking on SiO_2, which turns into suppressed blinking with long ON states and 2-14 folds enhanced PL intensities on Au nanorods. The single-particle PL and lifetime data are explained from the viewpoints of near-field plasmon-exciton coupling and suppressed photocharging.

C**hapter 5** focuses on analyzing coupling between the CdSe-ZnS QD exciton and plasmonic nanoc avities. Here, various plasmonic cavities are fabricated with the QDs inlaid in the cavities, which inclu de Au mirror-TiO_2-QD-Au NR (AT-QD-A) and Au mirror-QD-Au NR (A-QD-A). While the AT-QD-A cavity strongly quenched the QD emission, PL intensity enhancement is observed in the A-QD-A s ystem, where a newly formed low-lying plasmon-exciton hybridized state is the source of the enhance d PL intensity. The PL lifetime of the hybrid state is distinctly more extended than that of pristine Q Ds in single QD or film states. The mechanism of cavity-assisted enhanced PL intensity and delayed exciton recombination are discussed from the viewpoints of radiative and nonradiative relaxation proces ses from the initially populated and plasmon-coupled states.