学 位 論 文 内 容 の 要 約/Dissertation Summary

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

Semiconductor quantum dots (QDs) are nanoscale crystalline materials with tunable bandgaps and size-dependent optical and electronic properties, including high photoluminescence quantum yields (PLQYs), broad absorption, and narrow emission spectra. These features make them ideal for applications in solar cells, LEDs, lasers, photodetectors, and bioimaging, as demonstrated in studies on metal chalcogenide and metal halide perovskite QDs. However, multichannel excitonic recombination presents challenges, necessitating control over recombination pathways. Surface plasmon resonance (SPR), arising from the collective oscillation of free electrons in metallic nanoparticles (NPs) or nanostructures, can strongly interact with the excitonic fields of QDs, leading to enhanced absorption and emission. Despite significant progress, the underlying dynamics and efficiency of exciton-plasmon interactions, particularly at the single-particle level, are not fully understood.

This thesis demonstrates exciton-plasmon coupling in metal chalcogenide and halide perovskite QDs through single-particle PL blinking studies and ensemble-level measurements using plasmonic cavities. In Chapter 1, I introduce the theory of excitons, QDs, SPR, and exciton-plasmon coupling, followed by introducing relevant applications. Chapter 2 details the materials, methods, and instrumentation. Chapter 3 covers $MAPbI_3$ QD-Au nanorod (NR) systems, where QDs on SiO_2 exhibit slow blinking, but transition to rapid burst blinking with 3–13-fold PL enhancement on Au NRs, attributed to near-field coupling and resonant energy transfer. Chapter 4 investigates CdSe-ZnS QDs, which show suppressed blinking, prolonged ON states, and 2–14-fold PL enhancement on Au NRs due to exciton-plasmon coupling and reduced photochargin

g. Chapter 5 analyzes CdSe-ZnS QDs embedded in plasmonic cavities: Au mirror-TiO_2-QD-Au NR (AT-QD-A) and Au mirror-QD-Au NR (A-QD-A). While the ATQD-A cavity quenches emission, the A-QD-A configuration produces PL enhancement and a redshifted spectrum, attributed to a hybrid exciton-plasmon state. Cavity-assisted PL enhancement and delayed recombination are discussed.

This thesis reveals exciton-plasmon coupling dynamics in metal chalcogenide and halide perovskite QDs and provides strategies for improving PL efficiency.

Thesis summary

In Chapter 1, I introduced semiconductor QDs, surface plasmon resonance (SPR), and excitonplasmon coupling, as well as studies of QD-metal NP exciton-plasmon coupling at both the ensemble and single-particle levels. Owing to the quantum confinement effect and quantum size effect, QDs exhibit excellent optical properties such as broad absorption bands, narrow emission bands, high photoluminescence quantum yields (PLQYs), and anti-bleaching capability. Among the family of QDs, metal chalcogenide QDs and metal halide perovskite QDs are the most popular members. Metal chalcogenide QDs, usually composed of a divalent transition metal cation (Cd^{2+}, Pb^{2+}, Zn^{2+}) and a negatively charged divalent chalcogenide anion (S^{2-}, Se^{2-}, Te^{2-}), show an $A^{2+}B^{2-}$ composition. In contrast, metal halide perovskite QDs show an

$A^{+}B^{2+}(X^{-})_3$ composition, where A is a monovalent inorganic or organic cation [Cs^{+}, $CH_3NH_3^{+}$

(MA^{+}), $CH(NH_2)_2^{+}$ (FA^{+})], B is a divalent cation (Pb^{2+}, Sb^{2+}, Sn^{2+}), and X is a halide anion (Cl^{-}, Br^{-}, I^{-}). The bandgap of metal chalcogenide QDs is flexible through size and core-shell structure engineering, while the bandgap of metal halide perovskite QDs is also easily tuned by adjusting chemical components like halide composition. Both types of QDs are promising materials for the next-generation optical and electrical applications. However, the long PL decay with the multichannel exciton recombination process, with PL lifetimes ranging from ns to tens of ns, leads to low absorption efficiency. One of the most universal and effective methods to solve this is coupling with SPR.

SPR refers to the collective oscillations of the conduction band free electrons, typically in metal nanostructures, such as Au, Ag, Pt, Al, Cu, and Bi. The electron gas oscillation of metal nanostructures can be described by the Drude-Lorentz model. When the frequency of incident light matches the SPR oscillation frequency, a strong localized electromagnetic field forms, mediating coupled materials abso

rption, exciton generation, diffusion, and recombination. Generally, there are four coupling effects: “near-field coupling, far-field scattering, hot electron transfer, and energy transfer”. Depending on the coupling strength, weak coupling and strong c oupling regimes are classified, in which strong coupling generally requires a cavit y. Most studies about QD exciton-plasmon coupling focus on the ensemble level. S ingle-particle QDs blinking reveals exciton trapping-detrapping and charging-disch arging, providing an effective way for investigating exciton-plasmon coupling dyna mics. Notably, the details of the excitonplasmon coupling energy transfer, electron transfer, and exciton relaxation remain concealed. The PL modulation and exciton dynamics of QDs in a plasmonic cavity also require further investigation.

Chapter 2 details the materials, sample preparation, and instrumentation tech niques used in the thesis. First is the chemicals and reagents, followed by experi mental methods, including perovskite QDs synthesis and characterization, Au NRs film preparation, and plasmon cavity fabrication. A ligand-assisted reprecipitation (LARP) method and a modified spray method were employed to synthesize MAPb I_3 QDs. CdSe-ZnS QDs (CS QDs) and Au NRs are commercial products. Au NRs film was prepared by conjugating Au NRs on silanized coverslips via thiol groups. Plasmonic cavities were fabricated using a metal plasma sputtering system and an atomic layer deposition (ALD) system. The QDs were spread on bare coverslip s or Au film substrates for a single-particle blinking study. All the samples were characterized using UV-vis spectrophotometry, steady-state PL spectroscopy, single-particle microspectroscopy, time-resolved PL spectroscopy, transient absorption (T A) spectroscopy, transmission electron microscopy (TEM) & high-resolution scannin g transmission electron microscopy (HRSTEM). And the QD-plasmon near-field ele ctric field distributions were simulated using finite-difference time-domain (FDTD) simulations.

In Chapter 3, I presented the results and discussions of exciton-plasmon coup ling in halide perovskite $MAPbI_3$ QD-Au NR systems at the single-particle level. The QD-metal NP singleparticle blinking has already attracted various studies on different QDs and metal NP materials, which mainly focused on metal chalcogeni de QDs and showed blinking suppression. Studies on plasmon-assisted halide pero vskite QDs blinking remain largely unexplored. Since there are multiple exciton-pl asmon coupling effects, and the coupling is sensitive to time and distance, they m ay exhibit distinct blinking phenomena due to the strong affinity between halide i ons and plasmonic metals. The QDs and Au NRs absorption, PL, as well as TE M images, were first characterized, followed by single-particle blinking analysis. T he absorption of Au overlaps with the QD excitonic absorption band, enabling exc iton-plasmon coupling. The QD-Au sample absorption shows a shift from the Au

plasmonic band to the QD excitonic band, retaining the features of both bands, indicating hybridization of the plasmonic state and excitonic state. The single-particle samples were prepared by spraying $MAPbI_3$ precursor on SiO_2 or Au NRs (spray synthesis) or dropping a sub-nanomolar LARP-synthesized QD solution on SiO_2 or Au NRs, followed by dragging. QDs on SiO_2 illustrate slow ON-OFF blinking and low PL intensity. Interestingly, the QDs on Au NRs exhibit short-lived burst intense ON states. Statistical analysis of the blinking ON-OFF probability of 200 trajectories discloses significantly reduced ON and OFF times. Based on a diffusion-controlled electron transfer model (Marcus theory) for blinking exciton dynamics, the blinking ON-OFF time decrease suggests suppressed exciton trapping-detrapping and increased charging-discharging rate. In addition, the PL intensity from QDs to QD-Au systems was widely enhanced 3–13-fold, owing to the QDs to Au NRs position variation, which induced different coupling efficiencies. The position-dependent PL intensity enhancement was further proved through TEM, HRSTEM, and FDTD simulation study. Time-resolved PL study reveals decreased PL lifetime from QD (3.9 ± 0.8 ns) to QD-Au (2.2 ± 0.6 ns), indicating faster exciton relaxation rate with enhanced radiative recombination. Pump-probe TA study demonstrates accelerated ground state bleaching (GSB) recovery through exciton-plasmon coupling. The average GSB recovery time from QD to QD-Au decreased from 1131.7 ps to 46.4 ps. And the GSB recovery shows a fourth exponential feature, in which QD-Au first (τ_1), second (τ_2), third (τ_3), and fourth (τ_4) exponential recovery times are 400 fs, 8.0 ps, 220.0 ps, 787.7 ps, respectively. The characteristic τ_1, τ_2, τ_3, and τ_4 times are related to electron-electron scattering, electron-phonon coupling, phonon-phonon coupling, and accelerated exciton recombination, suggesting a phonon-assisted energy transfer process in which phonons compensate the energy difference between donor and acceptor. Based on the results, the dramatic change in blinking dynamics is attributed to QD-Au exciton-plasmon coupling near-field enhancement and plasmon resonance energy transfer induced biexciton state. The biexciton state either directly recombines to show bright biexciton emission or undergoes charging-discharging with nonradiative Auger recombination, showing frequent ON-OFF blinking. The unique PL intensity blinking change in the halide perovskite QD-Au system reveals dynamics of exciton-plasmon couplingdecoupling assisted by energy transfer, expected to improve the performance of halide perovskite QD devices.

In Chapter 4, exciton-plasmon coupling in the metal chalcogenide CdSe-ZnS QD (CS QD) and Au NR systems was examined. Previous studies on metal chalcogenide QDs have reported blinking suppression through thick shell capping, also known as gi

ant QDs, which face difficulties in controlling shell thickness from different materi als and low PLQY induced by excessively thick shells. Studies on CS QDs report ed blinking suppression through excitonplasmon coupling, while the mechanism of coupling, energy transfer, and electron transfer remains unknown. The QDs and Au NRs absorption, PL, as well as TEM images, were characterized first, followed by single-particle blinking analysis. The absorption of Au overlaps with the QD excitonic absorption band, enabling exciton-plasmon cou pling. The QD-Au sample absorption shows a shift from the Au plasmonic band t o the QD excitonic band, retaining features of both bands, which indicates hybridi zation of the plasmonic state and excitonic state. Single-particle samples were pre pared by dropping a sub-nanomolar commercial CS QD solution on SiO_2 or Au N Rs, followed by dragging. The CS QDs on a SiO_2 coverslip blink with a short ON -time and a widely distributed OFF-time, and illustrate extended ON-time with a sudden drop in intensity when coupled with Au NRs. Also, statistical analysis of the PL intensity trajectories was conducted. The ON-OFF time probability distrib utions, and PL intensity distributions demonstrate efficient exciton-plasmon couple d PL blinking suppression with prolonged ON time and decreased OFF time, 2–1 4-fold PL intensity enhancement, and significant lifetime decrease from QD (5.0 ± 0.4 ns) to QD-Au (1.7 ± 0.3 ns). The prolonged blinking ON time and decreased OFF time from the pristine short ON time and long OFF time imply trion neutr alization. QD-by-QD variations in the PL lifetime, intensity, and ON/OFF time on Au NRs suggest the relative position between QDs and Au NRs significantly affects the exciton-plasmon coupling efficiency, which was further veri fied using FDTD analysis. A mechanism was proposed in which Au electron tran sfer-assisted trion delocalization suppresses blinking, and plasmon near-field coupli ng is responsible for the PL intensity enhancement. Exciton-plasmon coupled PL i ntensity enhancement, lifetime decrease, and blinking suppression underscore an i ncreased light absorption rate and radiative rate along with improved PL properti es of QDs, which are essential for plasmonically-activated optical and photovoltaic devices.

In Chapter 5, exciton-plasmon coupling in plasmon cavities for CS QDs at th e ensemble level was investigated. Optical cavities can confine light into a small mode volume, increasing the density of states for light. And plasmonic materials c an combine with an optical cavity to form a plasmonic cavity, further improving t he optical properties of QDs, yielding ultrahigh PL intensity or even some nonline ar effects like amplified spontaneous emission or lasing. Two kinds of plasmonic c avities: an Au mirror-TiO_2-QDs-Au NRs (AT-QD-A) structure and an Au mirror-Q D-Au NRs (A-QD-A) structure were fabricated, forming simple Fabry–Pérot plasm

on cavities. Here, QDs were embedded in polymethyl methacrylate (PMMA) to pr otect it from charge transfer or energy transfer-induced quenching. The PMMA-pr otected QDs were incorporated into the middle between the Au mirror on the bot tom and the Au NRs on the top. Photons emitted from QDs were affected by bot h the Au NRs plasmon and the cavity mode. The QDs and Au NRs were first ch aracterized using absorption and PL spectra, as well as TEM imaging. The AT-Q D-A cavity exhibits a pronounced PL quenching effect, indicating significant photo n energy loss in the plasmon field. Conversely, the A-QD-A cavity enhances the QD PL and shows up to 2-fold enhancement with a redshifted hybrid state emiss ion (ca. 652 nm) compared to the pristine PL peak (ca. 624 nm). The PL lifetime s of the A-QD-A cavity single state (1.6 ns) and hybrid state (5.8 ns) are shorter than the pristine QD state (7.0 ns). A mechanism based on the QD energy band, the Au Fermi level, and the hybrid state energy level was established according t o the PL and lifetime variation. An excited electron from the QD CB can efficient ly transfer to the hybrid state and relax to the QD ground state with radiative r ecombination, which, combined with the plasmon energy transfer, provides enhanc ed PL intensity from the hybrid state. The transition to the hybrid state suppress es nonradiative recombination in the pristine QD state, thereby strengthening the emission intensity, decreasing the emission energy, and increasing the PL lifetime.

General conclusions

In summary, this thesis demonstrated exciton-plasmon coupling modulation of se miconductor quantum dot (QD) photoluminescence (PL) at both single-particle blin king and ensemble levels using plasmonic cavities. Single-particle blinking analysi s provided insights into exciton-plasmon dynamics, while plasmonic cavities signifi cantly enhanced coupling strength. Blinking behavior of $MAPbI_3$ perovskite QDs and CdSe-Z nS chalcogenide QDs was studied with and without gold (Au) plasmon coupling. $MAPbI_3$ QDs showed PL intensity enhancement with reduced ON-time and lifetime, whereas CdS e-ZnS QDs exhibited increased ON-time and shorter lifetime upon plasmon coupli ng.

CdSe-ZnS QDs in a plasmonic cavity displayed a hybridized exciton-plasmon st ate with delayed recombination and enhanced PL. $MAPbI_3$ QDs demonstrated long trapping-detrappi ng dominated blinking, which converted into short, intense bursts or frequent blin king on Au nanorods (NRs), varying with proximity to the plasmonic field, as sup

ported by FDTD simulations. ON-OFF probability analysis revealed faster carrier diffusion and enhanced charging-discharging blinking on Au NRs, with PL intensity enhanced 3–13-fold. Timeresolved PL and transient absorption indicated reduced lifetime and faster bleach recovery in QD-Au NR systems. The exciton-plasmon interaction was attributed to near-field coupling and plasmon-resonant energy transfer.

For CdSe-ZnS QDs on Au NRs, blinking suppression and 2–14-fold PL enhancement were observed, with shorter PL lifetimes and a proposed mechanism involving positive trion coupling with the plasmonic near-field. Ensemble-level analysis of core-shell QDs in plasmonic cavities revealed that while the AT-QD-A cavity quenched PL, the A-QD-A cavity induced PL enhancement, redshifted emission, and lifetime elongation—attributed to carrier transfer into a hybrid exciton-plasmon state.