Doctoral Thesis

Investigation of photoinduced electron transfer from CdSe-CdS and $FAPbBr_3$ nanocrystal assemblies to molecular acceptors

（CdSe-CdS および $FAPbBr_3$ ナノ結晶集合体から分子受容体への光誘起電子移動の研究）

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Abstract

Luminescent materials, such as halide perovskites (HPs) and chalcogenide quantum dots (QDs), are being widely studied for their potential to meet future energy harvesting and optoelectronic technologies. These materials exhibit exceptional brightness, stability, and longevity, making them highly promising for energy-efficient applications. One of their key attributes is the ability to facilitate photoinduced electron transport, which is critical for device development and performance. This thesis explores the process of photoinduced electron transfer from HP nanocrystals and chalcogenide QD assemblies to specific electron acceptor molecules. The study aims to understand how these materials interact with acceptors and how their structural and electrical features affect the electron transfer efficiency. The thesis is divided into five chapters, each providing insights into the role of these materials in device fabrication applications. Chapter 1 discusses the distinctive properties of PNCs and QDs, including the quantum confinement effect, synthesis methods, film preparation, absorption and emission properties, and charge carrier features. Chapter 2 details the preparation methodologies of PNCs and QDs, including synthesis procedures, co-aggregated assemblies, and instrumental techniques used. Chapter 3 focuses on photoinduced electron transfer from PNCs and their assemblies to specific acceptor molecules, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), fullerene (C_{60}), and a functionalized fullerene (C_{60}-RCOOH) ligand. The study shows that the development of assemblies is essential for promoting electron transfer, with $FAPbBr_3$ assemblies and co-aggregated assemblies showing significant electron transfer efficiency compared to single nanocrystals. Chapter 4 focuses on electron transfer capabilities of chalcogenide QD-based assemblies, using core/shell CdSe/CdS as the central unit. Chapter 5 covers a bio-inspired technique for generating water-soluble QD assemblies of mesoscopic size, highlighting the diversity of assembly processes and creating new opportunities for biocompatible optoelectronic applications. In summary, this thesis explores the assembly formation of perovskite materials and chalcogenide QDs, demonstrating their potential for practical applications and contributing to the understanding of material interactions.

Summary

Luminescent nanomaterials, particularly PNCs and chalcogenide QDs, are essential in advancing next-generation optoelectronic technologies. These semiconductor materials have attracted significant interest due to their superior photoluminescence (PL), high absorption coefficients, and

efficient charge carrier dynamics, making them promising candidates for applications in light-emitting diodes (LEDs), photovoltaics, optical detectors, and display technologies. Despite these advantages, the future of perovskite-based optoelectronics and photovoltaics relies on a deeper understanding of interfacial charge transfer mechanisms and long-range carrier diffusion. These processes play a crucial role in determining the efficiency and stability of perovskite-based devices. Addressing these challenges is essential for achieving commercial and industrial viability.

Chapter 1 begins with a detailed discussion of the historical background, fundamental structural features, and morphological characteristics of halide perovskite NCs and chalcogenide QDs, providing a comparative analysis of their unique properties. Various synthesis routes for both types of materials are explored, focusing on bottom-up approaches such as solution-phase synthesis, hot injection, and ligand-assisted reprecipitation. Additionally, the chapter examines self-assembly techniques used to fabricate thin films from these nanomaterials, which is crucial for integrating them into functional optoelectronic and photovoltaic devices. A significant portion of the chapter is dedicated to understanding the charge carrier dynamics in these materials, particularly in thin-film states. This includes discussions on interfacial charge transfer mechanisms, recombination pathways, and long-range carrier diffusion, which are vital factors influencing device performance. By examining these processes, the chapter highlights key challenges and opportunities for optimizing the efficiency and stability of optoelectronic and photovoltaic applications. Following this, the chapter explores various applications of halide perovskite NCs and chalcogenide QDs in cutting-edge technologies. These include high-efficiency solar cells, where these materials contribute to improved light absorption and charge transport; brilliant light-emitting devices with high color purity and tunable emission wavelengths; photodetectors with enhanced sensitivity and fast response times; and bioimaging applications leveraging their unique optical properties. The versatility and adaptability of these materials across different technological fields are emphasized, demonstrating their potential impact on future innovations.

Finally, the chapter concludes by outlining the motivation behind this research and defining the specific aims of this thesis. It underscores the significance of addressing fundamental scientific challenges related to charge carrier dynamics and material stability while advancing synthesis techniques for controlled nanomaterial fabrication. These efforts are essential for unlocking the

full potential of PNCs and chalcogenide QDs in commercial optoelectronic and photovoltaic applications.

Chapter 2 presents the synthesis and characterization methodologies employed for PNCs and QDs, as well as their assemblies, properties, and functionalities. It details the experimental techniques used to evaluate their structural, optical, and chemical characteristics. Two primary methods for PNC synthesis were ligand-assisted reprecipitation (LARP) for $MAPbBr_3$ and $FAPbBr_3$, and the hot injection method for $CsPbBr_3$. Additionally, CdSe/CdS QDs were synthesized and functionalized with carboxylic acid (QD-COOH) for comparative optical and electron transfer studies. Nanocrystal assemblies were prepared to enhance charge transport properties, with $FAPbBr_3$ assemblies incorporating electron acceptors and mesoscopic QD (ms-QD) structures synthesized *via* enzymatic processing. Thin films of PNCs were fabricated using drop-casting, and their surface morphology was analyzed through scanning transmission electron microscopy (STEM) and dynamic light scattering (DLS). The optical characterization of these materials was carried out using multiple spectroscopic techniques. UV-Vis Spectroscopy was used to examine the absorption properties, while fluorescence spectroscopy provided insights into photoluminescence behavior and electron transfer efficiency. Time-resolved spectroscopy, including quantaurus tau and picosecond laser (ps-Laser) technology, was utilized to investigate charge carrier dynamics and excited-state lifetimes in both solution and film states. Structural and chemical analysis was performed using nuclear magnetic resonance (NMR) spectroscopy (^{1}H-NMR, ^{13}C-NMR) to confirm molecular composition, electrospray ionization mass spectroscopy (ESI-MS) to determine molecular weights, and fourier-transform infrared spectroscopy (FT-IR) to analyze vibrational modes and functional groups. Furthermore, extensive studies on electron transfer kinetics were conducted, particularly focusing on charge transport mechanisms in nanocrystal assemblies. The synthesis of functionalized acceptor molecules, including C_{60} derivatives and azomethine ylide cycloaddition reactions, was explored to enhance the interaction between PNCs and QDs. The study of interfacial charge transfer in films was performed using time-correlated single photon counting (TCSPC), allowing for precise measurement of PL lifetimes. Additionally, the dynamic behavior of nanocrystals was assessed using the quantaurus tau (Q-Tau) system, revealing important insights into charge mobility and recombination processes.

Overall, this chapter establishes a robust experimental foundation for understanding the optical and electronic behavior of PNCs and QDs. Integrating advanced synthesis techniques with high-precision characterization methods provides valuable insights into their potential applications in optoelectronics, photovoltaics, and light-emitting devices. The results underscore the critical role of nanocrystal assemblies in enhancing charge transport and stability, paving the way for developing next-generation energy and display technologies. By optimizing the synthesis and characterization processes, this study contributes to the growing field of nanomaterials and their implementation in advanced photonic and electronic systems.

Chapter 3 explores the electron transfer mechanisms in PNC assemblies, particularly $FAPbBr_3$ PNCs, and their interactions with electron acceptor molecules in both solution and film states. The ability of perovskite nanocrystals to efficiently transport electrons is crucial for their potential applications in optoelectronic devices such as solar cells, LEDs, and other photonic technologies. PNCs exhibit tunable bandgaps, high absorption coefficients, and efficient charge carrier generation, making them promising candidates for electronic applications. However, uncontrolled aggregation and excess ligands can hinder efficient electron transfer. This study optimizes nanocrystal assembly formation to enhance charge transport by controlling molecular arrangements and surface interactions with electron acceptors.

$FAPbBr_3$ PNC assemblies were synthesized using the LARP method, ensuring uniform particle formation and stability. The synthesized assemblies were then studied in interactions with three electron acceptor molecules: P-C_{60}, C_{60}-RCOOH, and TCNQ. These acceptor molecules were chosen for their high electron affinity, allowing them to withdraw electrons from the perovskite donor system efficiently. The study was performed under solution and film-state conditions to analyze how molecular aggregation and environmental factors influence charge transport efficiency. PL quenching studies were conducted to examine the electron transfer efficiency in these systems. In the solution state, nanocrystal assemblies showed partial quenching due to ligand shielding effects, which prevented efficient interactions between donor and acceptor molecules. However, in the film state, co-aggregated assemblies exhibited complete PL quenching, suggesting highly efficient charge transfer facilitated by close packing and improved interfacial contact between donor and acceptor molecules. The time-resolved PL measurements and Stern-Volmer (S-V) analysis further confirmed that the observed quenching followed a static mechanism,

indicating the formation of stable donor-acceptor complexes rather than dynamic quenching events. Advanced characterization techniques such as STEM and DLS were employed further to understand these assemblies' structural and morphological aspects. These analyses demonstrated that controlled purification of PNC assemblies effectively reduced the presence of free ligands, thereby enhancing the accessibility of electron acceptors and promoting efficient charge transport. The ability to control molecular ordering within the assemblies was a key factor in optimizing the charge carrier dynamics. Comparative studies between different perovskite systems revealed that $FAPbBr_3$ PNCs exhibited superior charge transfer efficiency compared to $CsPbBr_3$ and $MAPbBr_3$. This improvement was attributed to the lower ligand density and enhanced crystallinity of $FAPbBr_3$, which provided better interfacial contact between the nanocrystals and electron acceptor molecules. In the co-aggregated film-state samples, acceptor molecules were incorporated within the assembly framework, leading to complete PL quenching and optimal electron transfer efficiency. This highlights the importance of molecular arrangement and surface ligand engineering in enhancing charge transport properties in perovskite-based systems.

The results of this study underscore the significance of controlled assembly formation in achieving efficient electron transfer in perovskite nanocrystals. The findings directly apply to high-performance optoelectronic devices, including solar cells, LEDs, and photocatalytic systems, where efficient charge transport is critical to device performance. By systematically tuning nanocrystal assembly structure and optimizing donor-acceptor interactions, this research provides valuable insights into the design principles of next-generation optoelectronic materials. Future advancements in nanocrystal assembly techniques could further improve the efficiency and stability of perovskite-based technologies, contributing to the development of more sustainable and energy-efficient electronic applications.

Chapter 4 explores the electron transfer dynamics in CdSe/CdS QD assemblies, focusing on their interactions with electron acceptors in both solution and assembled states. QDs have emerged as promising candidates for various optoelectronic applications due to their unique size-dependent optical and electronic properties, which allow tunable bandgaps, efficient charge carrier generation, and high photostability. However, the practical implementation of QDs in devices often encounters challenges such as aggregation, inefficient charge transport, and energy loss due to improper molecular interactions. This study employs controlled assembly techniques that enhance

charge mobility, stability, and overall performance to address these issues. By carefully tuning the structural and electronic properties of QD assemblies, optimizing their role in solar cells, LEDs, and photocatalytic applications was possible. QD assemblies were synthesized using 1,6-hexanedithiol (HDT) as a molecular crosslinker, which facilitated the formation of well-dispersed QD@HDT assemblies with improved interdot coupling. These assemblies were systematically characterized using various analytical techniques, including STEM and DLS, which confirmed their uniform size distribution and reduced agglomeration. The controlled organization of QDs in these assemblies is critical in enhancing charge transport efficiency by reducing the energy barriers that typically hinder electron flow in isolated QDs. By ensuring close packing and improved donor-acceptor proximity, these assemblies exhibit more effective charge transfer mechanisms than individual QDs. Fluorescence quenching experiments were performed to evaluate the efficiency of electron transfer in these QD@HDT assemblies using three different electron acceptors: P-C_{60}, C_{60}-RCOOH, and TCNQ. The fluorescence quenching studies revealed that QD@HDT assemblies displayed significantly enhanced PL quenching effects compared to isolated QDs, indicating a higher electron transfer efficiency. The presence of HDT as a crosslinker helped stabilize the QD assemblies and facilitated closer proximity between donors and acceptors, leading to improved charge transfer. Time-resolved photoluminescence (TRPL) measurements confirmed these observations, showing prolonged carrier lifetimes and reduced recombination losses in the assembled state. S-V analysis supported both static and dynamic quenching mechanisms, highlighting the formation of stable donor-acceptor complexes that enhance charge separation. Among the studied electron acceptors, P-C_{60} exhibited limited quenching effects in pristine QDs due to steric hindrance caused by surface ligands, restricting its accessibility to the QD surface. However, in QD@HDT assemblies, the quenching effect was significantly enhanced as the acceptor molecules could interact more efficiently with the donor QDs, leading to more effective charge separation. The functionalized fullerene C_{60}-RCOOH exhibited the strongest dynamic quenching effect due to its higher affinity for the QD surfaces, allowing for efficient charge transfer in the excited state. Meanwhile, TCNQ demonstrated both static and dynamic quenching behaviors, indicating its ability to form charge-transfer complexes with QD@HDT assemblies, further supporting the enhanced electron transfer properties of the assembled structures. These findings underscore the crucial role of interdot coupling and controlled assembly formation in optimizing charge transport efficiency in QD-based materials. The results suggest that by carefully

tuning nanostructures and donor-acceptor interactions, it is possible to significantly improve electron mobility, which is vital for advancing high-performance optoelectronic devices. Using molecular crosslinkers such as HDT provides a practical strategy for engineering QD-based materials with enhanced optoelectronic properties, paving the way for their integration into next-generation solar cells, LEDs, and other energy-harvesting technologies.

In conclusion, this study demonstrates that QD@HDT assemblies offer a significant improvement in electron transfer efficiency compared to isolated QDs, effectively addressing major challenges such as aggregation and inefficient charge transport. By strategically designing QD assemblies with controlled interfacial interactions, this research provides a foundation for future advancements in charge transport mechanisms and the developing of high-performance optoelectronic materials. These insights offer a promising direction for implementing QD assemblies in various technological applications, further pushing the boundaries of nanomaterial-based energy and photonic devices.

Chapter 5 investigates the electron transfer properties of ms-QD assemblies, emphasizing the role of collective interdot interactions in enhancing charge transport efficiency. Quantum dots are widely studied for their size-dependent optical and electronic properties, making them crucial for applications in solar energy harvesting, optoelectronics, and bioimaging. While single QDs have been extensively explored for their optical tunability and high photoluminescence quantum yield, their practical implementation in devices often faces challenges such as charge trapping, inefficient charge separation, and energy losses due to improper molecular interactions. QD assemblies introduce collective behaviors that significantly enhance charge transport and electron mobility by facilitating controlled electron hopping between neighboring quantum dots. This improvement is essential for the efficient function of next-generation optoelectronic devices such as light-emitting diodes, photodetectors, and solar energy conversion systems.

To address challenges in QD assembly synthesis, this study introduces the biocatalytic nanoparticle shaping (BNS) method, a bio-inspired enzymatic approach that facilitates the formation of well-dispersed ms-QD assemblies. This method offers a novel strategy to control QD aggregation while preserving their optical and electronic properties. The process involves the aggregation of QDs using oligo-L-lysine as a linker, forming large clusters (>1 μm), followed by controlled enzymatic cleavage using trypsin, breaking down these clusters into stable ms-QDs

(~84 nm in hydrodynamic diameter). This controlled fragmentation ensures excellent colloidal stability, enhances uniformity in structure and dispersion, and improves the connectivity between individual QDs within the assembly. The BNS approach is particularly advantageous for maintaining the electronic coupling necessary for enhanced charge transport, ensuring reproducibility and scalability, and overcoming previous limitations in QD assembly fabrication. Spectroscopic analyses confirmed that ms-QDs preserve the photophysical properties of individual QDs while exhibiting improved charge mobility due to reduced interdot spacing, which enhances electron transfer efficiency. This is critical because, in isolated QDs, charge carriers are often confined within individual particles, limiting their ability to participate in efficient transport mechanisms. By structuring these QDs into mesoscopic assemblies, the charge carrier diffusion length is extended, allowing for better electron mobility. This is particularly useful for improving efficiency in photovoltaics and light-emitting applications. PL quenching studies with electron acceptors, such as TCNQ, revealed rapid and efficient charge separation, an essential factor for optoelectronic applications that rely on controlled charge flow. TRPL studies demonstrated prolonged charge carrier lifetimes in ms-QDs, confirming that electron transfer dynamics are significantly improved compared to isolated QDs, which suffer from rapid non-radiative recombination. Extending charge carrier lifetime plays a key role in enhancing the performance of devices that require long-lived excitonic states. A comparative study with monomeric QDs (mono-QDs) revealed that ms-QDs exhibited significantly higher electron transfer efficiency due to their structured architecture, which minimizes energy barriers for charge transport. PL quenching studies demonstrated dynamic quenching in ms-QDs, indicating highly effective charge separation. In contrast, mono-QDs exhibited static quenching, suggesting weaker electron interactions due to the limited spatial proximity between donor and acceptor molecules. S-V analysis showed higher quenching rate constants for ms-QDs, further validating their enhanced electron transfer capabilities. These findings reinforce the importance of well-structured QD assemblies in achieving superior charge transport behavior, as opposed to relying solely on individual QDs, which may suffer from inefficient charge migration. The increased efficiency in ms-QDs can be attributed to the enhanced electronic coupling between QDs, allowing for a more seamless charge transfer process.

The findings of this study demonstrate that ms-QDs significantly enhance electron transfer efficiency compared to single QDs, making them promising candidates for advanced energy

conversion and optoelectronic applications. The BNS method revolutionizes QD assembly fabrication, providing a practical, scalable, and environmentally friendly approach for engineering high-performance charge transport materials. By establishing an efficient method for assembling QDs into well-ordered structures, this research provides a strong foundation for future advancements in quantum dot technology, ultimately paving the way for developing next-generation materials with optimized electronic properties. The findings underscore the importance of developing innovative strategies for QD assembly formation and charge transport optimization, offering new possibilities for improving the efficiency of solar cells, LEDs, and other optoelectronic devices that rely on controlled electron transfer processes.

General Conclusion

In conclusion, this thesis presents a comprehensive investigation into the interfacial electron transport processes in PNC and CdSe/CdS QD assemblies, emphasizing the influence of structural organization on charge transport efficiency. By exploring various electron acceptor molecules, including P-C_{60}, C_{60}-RCOOH, and TCNQ, the study elucidates the fundamental mechanisms governing electron transfer at the nanoscale. A combination of steady-state and time-resolved fluorescence spectroscopy techniques was utilized to analyze electron dynamics across different material configurations. A comparative analysis of perovskite systems, specifically $MAPbBr_3$ and $CsPbBr_3$, revealed poor electron transfer efficiency in solutions due to insulating surface ligands, such as oleic acid and oleyl amine. While stabilizing the nanocrystals in solution, these ligands act as barriers to efficient charge transport. However, $FAPbBr_3$ nanocrystals emerged as a superior alternative due to their exceptional optical properties, high photoluminescence quantum yield, and increased environmental stability. The study developed a controlled assembly strategy for $FAPbBr_3$ PNCs to overcome the limitations posed by surface ligands, enabling improved donor-acceptor interactions and enhancing electron transport. This strategy allowed the formation of well-structured assemblies, which facilitated efficient charge carrier movement, as confirmed through PL quenching and TCSPC measurements.

Additionally, the findings demonstrated the significance of co-aggregation in the film state, where interactions between PNCs and acceptor molecules resulted in complete PL quenching, confirming strong electronic coupling and aggregation-induced quenching effects. Parallel efforts in this research were directed at developing stable, well-dispersed CdSe/CdS QD assemblies using

the molecular crosslinker HDT. STEM imaging and DLS measurements verified the successful formation of these assemblies, which exhibited uniform dispersion and enhanced stability. Electron transfer studies using spectroscopic techniques confirmed that QD assemblies facilitated significantly higher charge transport efficiency than isolated QDs due to their structured architecture. The ability of these assemblies to bring quantum dots into proximity with electron acceptors resulted in enhanced charge separation and reduced recombination losses. Among the tested electron acceptors, C_{60}-RCOOH and TCNQ demonstrated the most substantial quenching effects, indicating their effectiveness in enabling efficient electron transfer. A key innovation in this work was developing a biocatalyst-driven method for synthesizing ms-QD assemblies via a biocatalytic nanoparticle-shaping approach. By utilizing oligo-lysine as a structural template, the study successfully created ms-QD ensembles (~84 nm in hydrodynamic size) that retained excellent optical and electronic properties. These assemblies exhibited high charge transport efficiency and strong interactions with electron acceptors, highlighting their potential for integration into advanced optoelectronic applications. The ability of these ms-QD assemblies to achieve effective electron transfer with TCNQ further underscores their applicability in next-generation energy harvesting and optoelectronic technologies.

Overall, this thesis provides fundamental insights into the electron transfer dynamics of PNC and QD assemblies, focusing on the role of surface ligands, structural organization, and electron acceptor interactions. The findings underscore the importance of controlled assembly strategies for optimizing charge transport in nanomaterials, paving the way for their application in photovoltaics, light-emitting devices, and nanoscale sensors. The work lays a strong foundation for further exploration and optimization of materials designed for high-performance optoelectronic devices, contributing valuable knowledge to advancing nanoscale charge transport mechanisms. This research highlights the transformative potential of engineered nanostructures in enabling efficient energy conversion and electronic applications, making significant strides in developing innovative light-harvesting and optoelectronic technologies.