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Author(s)	Bhagyashree Mahesha, Sachith
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Doctoral Thesis

Studies of photoinduced electron transfer and exciton dynamics in halide perovskite films and single particles

（ハロゲン化物ペロブスカイト膜と単一粒子における光誘起電子移動と励起子ダイナミクスの研究）

Division of Environmental Materials Science
Graduate School of Environmental Science
Hokkaido University

Bhagyashree Mahesha Sachith

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Summary of thesis

Halide perovskites emerge into a class of semiconductor materials for high-efficiency photovoltaic and optoelectronic devices. Their excellent optoelectronic properties, such as high photoluminescence quantum yields, halide- and size-dependent bandgap tuning, high absorption coefficients, high charge carrier mobility, and defect tolerance, have greatly attracted the entire semiconductor community. Nevertheless, understanding and optimizing the interfacial electron transfer and long-range charge carrier diffusion are important for future perovskite optoelectronics and photovoltaics. Chapter 1 briefly introduces halide perovskites, including their structure, synthesis, characterization, optical and charge carrier properties, and applications. At first, I introduce their history, summarizing their structures, chemical compositions, and stability factors. Next, I explain various perovskite nanocrystal synthesis methods to control the shape and dimensionality with suitable examples. The halide perovskite synthetic methods are critical to obtaining a pure and perfect crystal structure that can be stabilized with desired ligand molecules or doped with inorganic salts. High-quality perovskite nanocrystal fabrication is achieved at low temperatures because of its ionically bonded crystal structure.[1] One can achieve a majority carrier type and concentration by treating with different molecules (ligands or inorganic or organic salts).[2] However, the defect chemistry and physics for perovskites are still not understood precisely. Still, the energies from the vacancy-related defects are considered close to or within the band gaps. Halide perovskites can be synthesized by several straightforward, scalable, and cost-effective methods.[3-9] Particularly, researchers have developed several techniques for controlling the size, shape, and quality of their optical properties. High-quality bulk perovskite crystals (micro to millimeter-scale) can be readily crystallized by the inverse temperature crystallization technique (ITC),[10] solution temperature lowering method (STL),[11] anti-solvent vapor-assisted crystallization (AVC),[12] or laser trapping induced crystallization method.[13] On the other hand, halide perovskite nanocrystals (PNCs) can be obtained by hot injection,[3,6] a spray technique,[14] and the LARP method,[15] which are more convenient for fabricating thin-film devices.

The preparation methods for self-assembled perovskite nanocrystal thin films and different characterization techniques are discussed in the third section of this chapter. Further, I explain their bandgaps with the Jablonski diagram and the fundamentals of absorption and fluorescence spectroscopy. The band structures and the density of states substantially control the optical properties of halide perovskites. Hence it is necessary to explore their electronic structural disorders, dimensionality, and material composition to advance optoelectronic applications.[16-19] The main optoelectronic properties of halide perovskite, including the charge carrier mobility, excited-state lifetime, carrier recombination dynamics, and intrinsic carrier concentration, can be manipulated by controlling the structural framework. In halide perovskites, the conduction band minimum (CBM) is formed by hybridizing 6p-orbitals of Pb and s- and p-orbitals of halide. The valence band maximum (VBM) comprises 6p- and 6s-orbitals of Pb and s-and p-orbitals of halide. By varying the halide composition, one can easily tune the bandgap of these materials. For example,

the change in the halide from Cl to Br and Br to I increases the contribution of the halide p-orbitals to the VBM. Dynamically, this contribution favors the orbital mixing between the Pb s-orbital and halide p-orbital to a considerable extent.[20]

The fourth section describes the general charge carrier properties, including the charge carrier recombination mechanisms and their diffusion in single crystals and films. I provide the details of charge carrier diffusion lengths, time distributions, and diffusion coefficients. The precise knowledge of the charge carrier properties of halide perovskites is significantly important to advancing photovoltaic and optoelectronic applications. Halide perovskites are well known to exhibit long charge carrier lifetimes, high charge carrier mobility, and long-range carrier diffusion. The photoexcited excitons get converted into hot charge transfer states that dissociate into free charge carriers in about one ps or less by charge transport.[21,22] Numerous charge carrier lifetimes have been reported for halide perovskites. In particular, the electron quantum distribution, dielectric screening, exciton binding energy, exciton diffusion, etc., play a significant role in defining the lifetime. Also, the charge carrier properties and quantum confinement in single particles and closely packed films are explained. In the fifth section, I introduce the applications of halide perovskites to solar cells, photodetectors, and light-emitting diodes (LEDs) with details about the device architecture, carrier diffusion, and interfacial charge transfer mechanisms. Due to the excellent photovoltaic properties, such as large absorption cross-sections, wide and tunable bandgap, long-range charge carrier diffusion, and high PL quantum yield, halide perovskites have become an intense research subject for solar cells.[3,6,23] Today, halide perovskites are the most active semiconductor for solar cells. The rapid advances in the perovskite solar cell (PSC) technology are mainly due to their simple solution-processed preparation of high-quality thin films, the direct bandgap nature, high charge carrier mobility, and low Urbach energy. In the final section, I summarize my motivation for this research, then classify the specific objectives of this thesis.

The most appealing properties of halide perovskites, including solution processability, tunable emission wavelengths, high photoluminescence quantum yields, and high photostability, made them the current most actively investigated semiconductor materials today. Their outstanding optical properties, low Urbach energy, minimal Stokes shift, high charge carrier mobility, and long carrier diffusion lengths have led to lightning advances in photovoltaic and optoelectronic technologies. While the generation of excitons and their splitting into free charge carriers are very crucial for solar cells, the confinement and harvesting of such charge carriers in perovskite nanocrystal assemblies and single PNC remain largely concealed. The charge carrier diffusion in halide perovskite single crystals and films motivated me to develop closely-packed self-assembled PNC films with electron acceptor heterojunctions and understand the interfacial electron transfer and charge carrier diffusion dynamics. To compare the carrier/exciton lifetime and electron transfer rates of perovskite films with isolated PNCs, I investigated the exciton lifetime and electron transfer dynamics at single-particle levels. Also, to enhance the photoluminescence intensities and improve the excitation-emission cycle in single PNCs, I was motivated to interface PNCs with the surface plasmon resonance of Au nanoparticles.

Chapter 2 details the materials, samples, distinct experimental procedures, and instrumentation techniques in this thesis. A brief overview of the chemicals and materials is followed by the perovskite nanocrystal synthesis and their characterization. I employed hot injection, ligand-assisted reprecipitation, and modified spray techniques to synthesize $CsPbBr_3$, $MAPbBr_3$, and $FAPbBr_3$ nanocrystals. These methods provided narrow and uniform size distributed perovskite nanocrystals. The synthesized perovskite nanocrystals dispersed in toluene were processed into single-particle samples or thin films by drop-casting, spin-coating, or spray techniques. Au nanoparticle films were prepared by sputter-coating. Scanning transmission electron microscopy, scanning electron microscopy, and a focused ion beam system was used to characterize the perovskite and Au nanoparticle sizes and perovskite film thicknesses. The steady-state UV-vis absorption spectroscopy was utilized to characterize the excitonic bands of the synthesized perovskite nanocrystals. The relaxation processes of the excitons from the excited to the ground states can be determined by this technique. The emission features were studied using steady-state and time-resolved techniques. Similarly, the distance-dependent charge carrier diffusion and electron transfer dynamics in electron D-A systems were also analyzed using this technique. The motorized stage with a micrometer was utilized in the distance-dependent PL measurements.

The PL decay profiles were fitted using the third exponential equation (1):

$$\gamma(t) = \alpha_0 + \alpha_1 e^{(-t/\tau 1)} + \alpha_2 e^{(-t/\tau 2)} + \alpha_3 e^{(-t/\tau 3)} \qquad (1)$$

where α_0 is a constant, α_1, α_2, and α_3 are the amplitudes, and τ_1, τ_2, and τ_3 are the different lifetime components. Generally, the initial component arises from radiative recombination, and the other two components are from nonradiative recombination. I calculated the intensity average PL lifetimes of the samples using equation (2):

$$\Sigma\ \alpha_n\tau_n\ /\ \Sigma\ \alpha_n \qquad (2)$$

The structural properties were analyzed by scanning transition electron microscopy. I used a single-particle fluorescence microspectroscopy system with an EMCCD to understand the single-particle level exciton plasmon coupling and electron transfer. The exciton relaxation, plasmon coupling, and electron transfer dynamics of perovskite films were further analyzed using transient absorption spectroscopy.

Photoinduced electron transfer (PET) studies in perovskite nanocrystal-based electron donor-acceptor (D-A) systems receive great momentum, owing to their potential application to solar cell technology. Nevertheless, radiative and nonradiative carrier losses adversely affect the energy conversion efficiency in thick perovskite films. Therefore, it is particularly important to investigate the photoinduced electron transfer dynamics, carrier trapping, and relaxation process at perovskite-based donor-acceptor interfaces. Chapter 3 demonstrates long-range charge carrier diffusion and distance-dependent electron transfer in heterojunction films of cesium or formamidinium lead bromide ($Cs/FAPbBr_3$) PNCs and C_{60} or TiO_2. PET is the fundamental process in a solar cell. In principle, the photogenerated excitons in PNCs split into free carriers, and it's necessary to capture them more efficiently using hole and electron transport layers (ETLs). This was first achieved in 2015 by Snaith and co-workers[24] developed efficient PSCs using solution spin-coated C_{60} in regular n-i-p structures. They found the effectiveness of C_{60} as an ETL, which shows excellent electron extraction ability and increases the long-term performance of PSCs. This opened a door for developing regular n-i-p high-performance PSCs. Later many reports showed higher power conversion efficiencies in PSC by achieving charge separation using different ETLs. For example, Long and co-workers[25] used TiO_2 as an electron acceptor in a PSC and reported the high efficiency contributed by the ultrafast interfacial charge separation. The electron injection is fast at the perovskite-electron acceptor (e.g., TiO_2) interface. In a subsequent study, Chen and co-workers[26] used a high-quality polycrystalline SnO_2 film as the electron-transport layer (ETL) in an n-i-p-type PSC. They reported the best solar cells fabricated using these layers and achieved 20.52% power conversion efficiency, which was among the best in the planar n–i–p-type PSCs class. Recently, Xu and co-workers[27] used four types of ETLs, i.e., compact titanium dioxide (c-TiO_2), mesoporous titanium dioxide (m-TiO_2) composite layers, C_{60}, and c-TiO_2 and C_{60}. The c-TiO_2-based PSCs showed higher efficiency (20.15%) than other ETL materials. The champion device efficiency using the C_{60} ETL achieved before was 17.15%. These outcomes encouraged me to evaluate the interfacial region between the PNCs and electron acceptors and control the electron transfer from perovskite films by controlling the diffusion of photogenerated charge carriers.

I synthesized $CsPbBr_3$ and $FAPbBr_3$ PNCs by the hot-injection and LARP methods, respectively, and their thin films with different thicknesses were prepared by ligand-assisted assembly formation. To understand the electron transfer, the PL quenching experiment was performed for Cs/$FAPbBr_3$ PNC solution by treating them with a C_{60} solution (in toluene) in 25 µM portions in a stepwise fashion. PET and charge separation were confirmed from the PL lifetime, PL intensity, and TA spectra in the solution phase. Subsequently, I prepared the D-A heterojunction films with Cs/$FAPbBr_3$ PNCs as the donor and C_{60} or TiO_2 as the acceptor. To understand the carrier collection as a function of the distance and thicknesses in the films, I conducted distance-dependent PL experiments by systematically moving the excitation from the perovskite to D-A interface region. Interestingly, the carrier recombination rates at different distances reveal the complete electron transfer and emission quenching within 100 µm of the interface. Radiative recombination dominates the electron transfer process while moving the interface away from the excitation center. Also, the electron transfer becomes negligibly small at 800 µm or beyond the interface.

While lead halide perovskites are exciting materials for photovoltaic and optoelectronic devices, the potential applications of ligand-assisted self-assembly and close-packed PNCs to various devices are yet to be explored. In this chapter, I summarized the long-range carrier migration and interfacial electron transfer in D-A systems. I found longer PL lifetimes for PNCs in a film than in a solution, indicating the long-range diffusion of photogenerated carriers among PNCs. On the other hand, the adsorption of C_{60} molecules onto the hydrophobic surface of PNCs in a solution resulted in the PL quenching with constant PL lifetime values at all acceptor concentrations, suggesting a static electron transfer. The interfacial electron transfer was obvious from forming the C_{60} anion radical. Interestingly, as I moved the pump-probe region towards the interface in a D-A film, at every 100 µm distance, the PL lifetime decreased gradually and became saturated near the interface. Therefore, the interfacial electron transfer is distance-dependent, evident from a decrease in the PL lifetime by moving the carrier generation center towards the interface. I believe this study about thin films and distance-dependent carrier capturing enables one to improve the electronic and photovoltaic applications of PSCs.

Halide PNCs are promising materials for energy harvesting and light-emitting applications. While the perovskite-based electron donor-acceptor interfaces offer unique control of the optical bandgap throughout the visible region of the electromagnetic spectrum, nonradiative losses adversely affect the charge injection efficiency. Thus, electron D-A systems composed of perovskite nanocrystals receive considerable attention. In chapter 4, I demonstrate the real-time electron transfer of single perovskite nanocrystals treated with acceptors such as tetracyanobenzene (TCNB) and tetracyanoquinodimethane (TCNQ) molecules. I reveal the dynamics and rates of electron transfer through the real-time blinking suppression and enhancement of single PNCs treated with TCNQ or TCNB molecules. At first, I confirmed the electron transfer feasibility by measuring steady-state absorption spectra, which evidenced the formation of TCNQ radical anion at 730 nm. Also, I calculated the Gibbs free energy change electron transfer for PNC-acceptor systems by measuring the oxidation and reduction potentials of the donors and acceptors. Later, I recorded the PL lifetime, PL intensity, and PL blinking trajectories of single PNCs before or after the treatment with TCNB/TCNQ. TCNB/TCNQ molecules quenched the PL intensities of PNCs accompanied by decreases in the PL lifetimes in a solution, revealing a dynamic electron transfer. I investigate the blinking of single PNCs before or after the treatment with TCNB/TCNQ. The blinking was suppressed in real-time; the PL intensity trajectory of a single PNC with TCNB shows a stable off-state, accompanied by rare PL blinking events, whereas a PNC with TCNQ showed long-living OFF and intermittent ON events. After analyzing several hundred single PNCs before or after treatment with TCNB/TCNQ, the ON/OFF-time probability distributions are summarized.

Recently, the electron D-A systems made of TCNQ/TCNB have received considerable attention because of their high electron affinities. For example, Hye *et al.*[28] used TCNQ as an electron scavenger in photoelectrochemical studies and reported the rapid electron transfer from an electrode to TCNQ. Here the electron transfer was studied based on *in-situ* spectro-electrochemical methods. Chang *et al.*[29] prepared a layer-by-layer graphene/TCNQ anode for organic solar cells, where TCNQ molecules were tethered between two graphene layers. The strong electron affinity of TCNQ helped in achieving a high PCE and became attractive for next-generation solar cells. In a comparable study, Yoshiyuki *et al.*[30] successfully measured the electron transfer for CdTe nanocrystal/TCNB D-A system using steady-state and time-resolved PL spectroscopy. They observed PL quenching of CdTe nanocrystals by TCNB through static electron transfer. The above works explain the importance of TCNQ/TCNB as an electron scavenger. However, PET can differ for every single PNC in films, depending on their heterogeneity.[31] Therefore, understanding the electron transfer process at the single-particle level can provide further insights into the construction of efficient electron donor-acceptor (D-A) interfaces composed of halide perovskites.

The photoexcited state properties of single PNCs have been widely investigated concerning PL fluctuations (blinking). PL blinking is one of the most critical issues affecting the efficient capturing of electrons.[32] Generally, the bright state in the PNC blinking is called the ON state, and the dark state is OFF. Two approaches have been widely accepted to understanding the PL blinking of PNCs: i) the charging/discharging model (type-A)[33] and ii) the activation/deactivation of nonradiative recombination centers (type-B).[34] The ionized/charged state can initiate nonradiative Auger recombination processes (type-A blinking) *via* the flow of the exciton energy to a third carrier (either an electron or a hole).[35] In type-B blinking, the presence of multiple recombination centers causes PNC to undergo activation and deactivation mechanism. The shallow traps or short-lived traps in the bandgap called multiple recombination centers regulate the nonradiative recombination rates. The electrons trapped in the surface trap state can transfer to the electron acceptor at a heterojunction by channeling the neutralization of charged PNCs through the acceptor resulting in blinking suppression. Nevertheless, PL quenching occurred in most particles; for example, TiO_2 was used as an electron acceptor to suppress the PL blinking of CdSe/ZnS QDs.[36] The nonradiative carrier recombination in QDs was changed into electron transfer to TiO_2 nanoparticles, evident from the decrease in the PL intensity. Despite such examples, a high electron transfer rate for a PNC-based D-A interface can be valuable for developing next-generation PSC devices.

Lead halide PNCs are emerging into a class of cutting-edge materials for high-efficiency solar cells and light-emitting devices. In this chapter, I revealed the dynamics of photoinduced electron transfer through real-time blinking analysis of single PNCs. The negative value of Gibbs's free energy change helped predict the feasibility of electron transfer. The electron transfer was evident from decreased PL intensity and lifetime of PNCs treated with acceptors. The decreased truncation times of PNCs treated with TCNB suggest increases in the ionization probability, which is attributed to electron transfer to TCNB. This study highlights the significance of an electron D-A interface at a single NC level.

Localized surface plasmon resonance (LSPR) of metal nanoparticles significantly improves the optical properties of halide perovskite nanocrystals. However, plasmon-induced photoluminescence enhancement is still underutilized because of not fully understand the origin of plasmon-induced photoluminescence enhancement. In Chapter 5, I prepared the heterostructures of PNCs on Au NPs, analyzed the exciton-plasmon interaction, and validated the photophysical properties of PNCs. The PNCs on an Au NP film show a strong PL intensity enhancement of up to 12-fold at the single-particle level. I also study the dynamics of PL intensity enhancement or quenching of single PNCs with ligand discrimination between the active and inactive chemical coupling of Au-Br. First, I synthesized two different $MAPbBr_3$ PNCs and prepared the hetero-nanostructure films with Au NPs and PNCs. I confirm the LSPR coupling with excitons at a single particle level by PL blinking, PL intensity, and PL lifetime studies. By considering the dot-by-dot variations of the ON- and OFF-time distributions, I perform the statistical evaluation of the ON/OFF-time probability distributions for more than 450 PNCs on an Au or a glass substrate to understand the differences in the blinking behavior.

The perovskites-metal composites can generate strong light-matter coupled states due to the coupling of the excitons of perovskites and the LSPR of the metal NPs. Therefore, understanding the mechanism of PNCs coupled with the LSPR at the single-particle level can provide further insights into the fundamental process of the exciton-plasmon interactions. To date, this plasmon coupled PL fluctuations (blinking), and the origins of enhancement and quenching in PNC-Au nanostructures remain largely unknown. LSPR-induced optical properties improvement has been reported not only for perovskites but also for organic dye molecules and conventional chalcogenide semiconductor quantum dots (QDs). In the early investigations of dye molecules' plasmon-induced PL enhancement, Knoll et al.[37] reported PL enhancement of cadmium arachidate monolayer coated on a silver grating. Kinkhabwala et al.[38] reported the enhancement of single-molecule fluorescence up to 1,340 times by using an Au nanoantenna. For conventional semiconductor QDs, Ma et al.[39] reported the PL intensity enhancement for single CdSe multi-shell nanocrystal on the Au NP film up to 3 times. Fu et al.[40] reported blinking suppression and PL intensity enhancement for streptavidin functionalized CdSe/ZnS QDs linked to biotin-coated Ag NPs. These plasmon-induced PL intensity enhancements are based on energy transfer from LSPR to fluorophores or Purcell effects, an increase of the spontaneous emission rate caused by the plasmon-induced strong near field (hot spots). The PL intensity enhancement by energy transfer and PL quenching by energy or charge transfer, depending on the distance between a fluorophore and the plasmonic substrate.

In this chapter, I report the dynamics of plasmon-induced photoluminescence enhancement and quenching for perovskite nanocrystals with ligand discrimination between the active and inactive chemical coupling of Au-Br bonding. The interaction significantly changes the optical properties of methylammonium lead bromide perovskite nanocrystals with adjacent localized surface plasmon resonance of Au nanoparticles. The dynamics of photoluminescence enhancement and quenching are examined at the single-particle level. A decrease in the photoluminescence lifetime accompanies a significant increase in OFF intervals. The direct synthesis of $MAPbBr_3$ perovskite nanocrystals on Au-nanoparticles increases the total radiative decay rate by the resonance caused by chemical coupling between Au-Br and the surface plasmon resonance. This change in the radiative rate increases single particles' photoluminescence intensity and OFF times. The PL enhancement is attributed to Au-Br-assisted, LSPR-mediated energy transfer from Au to PNCs. Fluctuations in the PL intensity are attributed to transient decoupling of the Au-Br interactions.

References

1. Li, X.; Bi, D.; Yi, C.; Décoppet, J. D.; Luo, J.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M. A Vacuum Flash-Assisted Solution Process for High-Efficiency Large-Area Perovskite Solar Cells. *Science* **2016**, *353*, 58–62.
2. Liu, M.; Johnston, M. B.; Snaith, H. J. Efficient Planar Heterojunction Perovskite Solar Cells by Vapour Deposition. *Nature* **2013**, *501*, 395–398.
3. Chouhan, L.; Ghimire, S.; Subrahmanyam, C.; Miyasaka, T.; Biju, V. Synthesis, Optoelectronic Properties and Applications of Halide Perovskites. *Chem. Soc. Rev.* **2020**, *49*, 2869–2885.

4. Shamsi, J.; Urban, A. S.; Imran, M.; De Trizio, L.; Manna, L. Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties. *Chem. Rev.* **2019**, *119*, 3296–3348.
5. Dong, Y.; Zou, Y.; Song, J.; Song, X.; Zeng, H. Recent Progress of Metal Halide Perovskite Photodetectors. *J. Mater. Chem. C* **2017**, *5*, 11369–11394.
6. Zhu, X.; Ge, L.; Wang, Y.; Li, M.; Zhang, R.; Xu, M.; Zhao, Z.; Lv, W.; Chen, R. Recent Advances in Enhancing and Enriching the Optical Properties of Cl-Based $CsPbX_3$ Nanocrystals. *Adv. Opt. Mater.* **2021**.
7. Leng, J.; Liu, J.; Zhang, J.; Jin, S. Decoupling Interfacial Charge Transfer from Bulk Diffusion Unravels Its Intrinsic Role for Efficient Charge Extraction in Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2016**, *7*, 5056–5061.
8. Scheidt, R. A.; Kerns, E.; Kamat, P. V. Interfacial Charge Transfer between Excited $CsPbBr_3$ Nanocrystals and TiO_2: Charge Injection versus Photodegradation. *J. Phys. Chem. Lett.* **2018**, *9*, 5962–5969.
9. Xu, D.; Liu, D.; Xie, T.; Cao, Y.; Wang, J. G.; Ning, Z. J.; Long, Y. T.; Tian, H. Plasmon Resonance Scattering at Perovskite $CH_3NH_3PbI_3$ Coated Single Gold Nanoparticles: Evidence for Electron Transfer. *Chem. Commun.* **2016**, *52*, 9933–9936.
10. Forde, A.; Kilin, D. Hole Transfer in Dye-Sensitized Cesium Lead Halide Perovskite Photovoltaics: Effect of Interfacial Bonding. *J. Phys. Chem. C* **2017**, *121*, 20113–20125.
11. Luo, X.; Liang, G.; Han, Y.; Li, Y.; Ding, T.; He, S.; Liu, X.; Wu, K. Triplet Energy Transfer from Perovskite Nanocrystals Mediated by Electron Transfer. *J. Am. Chem. Soc.* **2020**, *142*, 11270–11278.
12. Sachith, B. M.; Okamoto, T.; Ghimire, S.; Umeyama, T.; Takano, Y.; Imahori, H.; Biju, V. Long-Range Interfacial Charge Carrier Trapping in Halide Perovskite-C_{60} and Halide Perovskite-TiO_2 Donor-Acceptor Films. *J. Phys. Chem. Lett.* **2021**, 12, 8644–8651.
13. Wojciechowski, K.; Stranks, S. D.; Abate, A.; Sadoughi, G.; Sadhanala, A.; Kopidakis, N.; Rumbles, G.; Li, C.; Friend, R. H.; Jen, A. K.; Snaith, H. J. Heterojunction Modi Fi Cation for Highly Solar Cells. *ACS Nano* **2014**, *8*, 12701–12709.
14. Jiang, Q.; Ni, Z.; Xu, G.; Lin, Y.; Rudd, P. N.; Xue, R.; Li, Y.; Li, Y.; Gao, Y.; Huang, J. Interfacial Molecular Doping of Metal Halide Perovskites for Highly Efficient Solar Cells. *Adv. Mater.* **2020**, *32*, 1–10.
15. Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. Il. Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. *Nature* **2015**, *517*, 476–480.
16. Brennan, M. C.; Forde, A.; Zhukovskyi, M.; Baublis, A. J.; Morozov, Y. V.; Zhang, S.; Zhang, Z.; Kilin, D. S.; Kuno, M. Universal Size-Dependent Stokes Shifts in Lead Halide Perovskite Nanocrystals. *J. Phys. Chem. Lett.* **2020**, *11*, 4937–4944.
17. Jeong, J.; Kim, M.; Seo, J.; Lu, H.; Ahlawat, P.; Mishra, A.; Yang, Y.; Hope, M. A.; Eickemeyer, F. T.; Kim, M.; Yoon, Y. J.; Choi, I. W.; Darwich, B. P.; Choi, S. J.; Jo, Y.; Lee, J. H.; Walker, B.; Zakeeruddin, S. M.; Emsley, L.; Rothlisberger, U.; Hagfeldt, A.; Kim, D. S.; Grätzel, M.; Kim, J. Y. Pseudo-Halide Anion Engineering for α-$FAPbI_3$ Perovskite Solar Cells. *Nature* **2021**, *592*, 381–385.
18. Bi, E.; Chen, H.; Xie, F.; Wu, Y.; Chen, W.; Su, Y.; Islam, A.; Grätzel, M.; Yang, X.; Han, L. Diffusion Engineering of Ions and Charge Carriers for Stable Efficient Perovskite Solar Cells. *Nat. Commun.* **2017**, *8*, 15330.
19. Zhumekenov, A. A.; Saidaminov, M. I.; Haque, M. A.; Alarousu, E.; Sarmah, S. P.; Murali, B.; Dursun, I.; Miao, X. H.; Abdelhady, A. L.; Wu, T.; Mohammed, O. F.; Bakr, O. M. Formamidinium Lead Halide Perovskite Crystals with Unprecedented Long Carrier Dynamics and Diffusion Length. *ACS Energy Lett.* **2016**, *1*, 32–37.
20. Mandal, S.; Tkachenko, N. V. Multiphoton Excitation of $CsPbBr_3$ Perovskite Quantum Dots (PQDs): How Many Electrons Can One PQD Donate to Multiple Molecular Acceptors? *J. Phys. Chem. Lett.* **2019**, 2775–2781.
21. Lu, H.; Chen, X.; Anthony, J. E.; Johnson, J. C.; Beard, M. C. Sensitizing Singlet Fission with Perovskite Nanocrystals. *J. Am. Chem. Soc.* **2019**, *141*, 4919–4927.

22. Li, Z.; Wang, R.; Xue, J.; Xing, X.; Yu, C.; Huang, T.; Chu, J.; Wang, K. L.; Dong, C.; Wei, Z.; Zhao, Y.; Wang, Z. K.; Yang, Y. Core-Shell ZnO@SnO_2 Nanoparticles for Efficient Inorganic Perovskite Solar Cells. *J. Am. Chem. Soc.* **2019**, *141*, 17610–17616.
23. Rhee, S.; An, K.; Kang, K. T. Recent Advances and Challenges in Halide Perovskite Crystals in Optoelectronic Devices from Solar Cells to Other Applications. *Crystals* **2021**, *11*, 39.
24. Wojciechowski, K.; Leijtens, T.; Siprova, S.; Schlueter, C.; Hörantner, M. T.; Wang, J. T. W.; Li, C. Z.; Jen, A. K. Y.; Lee, T. L.; Snaith, H. J. C_{60} as an Efficient N-Type Compact Layer in Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2015**, *6*, 2399–2405.
25. Long, R.; Fang, W. H.; Prezhdo, O. V. Strong Interaction at the Perovskite/TiO_2 Interface Facilitates Ultrafast Photoinduced Charge Separation: A Nonadiabatic Molecular Dynamics Study. *J. Phys. Chem. C* **2017**, *121*, 3797–3806.
26. Chen, C.; Jiang, Y.; Guo, J.; Wu, X.; Zhang, W.; Wu, S.; Gao, X.; Hu, X.; Wang, Q.; Zhou, G.; Chen, Y.; Liu, J. M.; Kempa, K.; Gao, J. Solvent-Assisted Low-Temperature Crystallization of SnO_2 Electron-Transfer Layer for High-Efficiency Planar Perovskite Solar Cells. *Adv. Funct. Mater.* **2019**, *29*, 1–9.
27. Xu, C.; Zhang, Y.; Luo, P.; Sun, J.; Wang, H.; Lu, Y. W.; Ding, F.; Zhang, C.; Hu, J. Comparative Study on TiO_2 and C_{60} Electron Transport Layers for Efficient Perovskite Solar Cells. *ACS Appl. Energy Mater.* **2021**, *4*, 5543–5553.
28. Jeong, H. W.; Zsigmond, T. S.; Samu, G. F.; Janáky, C. Sacrificial Agent Gone Rogue: Electron-Acceptor-Induced Degradation of CsPbBr3 Photocathodes. *ACS Energy Lett.* **2022**, *7*, 417–424.
29. Hsu, C. L.; Lin, C. Te; Huang, J. H.; Chu, C. W.; Wei, K. H.; Li, L. J. Layer-by-Layer Graphene/TCNQ Stacked Films as Conducting Anodes for Organic Solar Cells. *ACS Nano* **2012**, *6*, 5031–5039.
30. Nonoguchi, Y.; Nakashima, T.; Kawai, T. Low-Temperature Observation of Photoinduced Electron Transfer from CdTe Nanocrystals. *J. Phys. Chem. C* **2009**, *113*, 11464–11468.
31. Liu, X.; Zhao, H.; Wei, L.; Ren, X.; Zhang, X.; Li, F.; Zeng, P.; Liu, M. Ligand-Modulated Electron Transfer Rates from $CsPbBr_3$ Nanocrystals to Titanium Dioxide. *Nanophotonics* **2021**, *10*, 1967–1975.
32. Chouhan, L.; Ito, S.; Thomas, E. M.; Takano, Y.; Ghimire, S.; Miyasaka, H.; Biju, V. Real-Time Blinking Suppression of Perovskite Quantum Dots by Halide Vacancy Filling. *ACS Nano* **2021**, *15*, 2831–2838.
33. Yuan, G.; Gómez, D. E.; Kirkwood, N.; Boldt, K.; Mulvaney, P. Two Mechanisms Determine Quantum Dot Blinking. *ACS Nano* **2018**, *12*, 3397–3405.
34. Trinh, C. T.; Minh, D. N.; Ahn, K. J.; Kang, Y.; Lee, K. G. Organic-Inorganic $FAPbBr_3$ Perovskite Quantum Dots as a Quantum Light Source: Single-Photon Emission and Blinking Behaviors. *ACS Photonics* **2018**, *5* (12), 4937–4943.
35. Trinh, C. T.; Minh, D. N.; Ahn, K. J.; Kang, Y.; Lee, K. G. Verification of Type-A and Type-B-HC Blinking Mechanisms of Organic–Inorganic Formamidinium Lead Halide Perovskite Quantum Dots by FLID Measurements. *Sci. Rep.* **2020**, *10*, 1–8.
36. Hamada, M.; Nakanishi, S.; Itoh, T.; Ishikawa, M.; Biju, V. Blinking Suppression in CdSe / ZnS Single. *ACS Nano* **2010**, *4*, 4445–4454.
37. Knoll, W.; Philpott, M. R.; Swalen, J. D.; Girlando. A. Emission of light from Ag metal gratings coated with dye monolayer assemblies. *J. Chem. Phys.* **1981**, *75*, 4795–4799.
38. Kinkhabwala, A. *et al.* Large single-molecule fluorescence enhancements produced by a bowtie nanoantenna. *Nat. Photonics* **2009**, *3*, 654–657.
39. Ma, X.; Tan, H.; Kipp, T.; Mews, A. Fluorescence Enhancement, Blinking Suppression, and Gray States of Individual Semiconductor Nanocrystals Close to Gold Nanoparticles. *Nano Lett.* **2010**, *10*, 4166–4174.
40. Fu, Y.; Zhang, J.; Lakowicz, J. R. Silver-Enhanced Fluorescence Emission of Single Quantum Dot Nanocomposites. *Chem. Commun.* **2009**, 3, 313–315.