

Abstract

All-inorganic lead halide perovskite nanocrystals (CsPbX_3 , where $\text{X} = \text{Cl}, \text{Br}, \text{and I}$) have emerged as a highly promising class of semiconductor materials for next-generation optoelectronic devices, including solar cells, light-emitting diodes (LEDs), and photodetectors. Their exceptional properties, such as high absorption coefficients, long charge carrier diffusion lengths, tunable bandgaps, narrow emission linewidths, and defect-tolerant electronic structures, make them superior to many conventional semiconductor systems. Among the different compositions, CsPbI_3 nanocrystals have attracted particular attention due to their optimal bandgap ($\sim 1.7\text{--}1.8\text{ eV}$), which aligns well with the peak of the solar spectrum, rendering them highly suitable for photovoltaic and light emitting diode applications. However, despite these advantages, the practical implementation of CsPbI_3 nanocrystals is significantly hindered by their intrinsic phase instability and rapid degradation under ambient conditions, particularly due to moisture, oxygen exposure, and thermal fluctuations. This instability results in a phase transition from the photoactive cubic, α -phase to the non-perovskite δ -phase, leading to severe deterioration in optical and electronic properties.

In this dissertation, comprehensive and systematic approaches have been adopted to address the stability challenges of CsPbX_3 nanocrystals through multiple strategies, including doping engineering, ligand-assisted surface passivation, defect modulation, and post-synthetic structural recovery. Initially, high-quality CsPbBr_3 and CsPbI_3 nanocrystals were synthesized via a modified hot-injection method, enabling precise control over nucleation and growth kinetics. These nanocrystals were subsequently employed as sensitizers in nanocrystal-sensitized solar cells (NCSSCs). Comparative analysis revealed that CsPbI_3 based devices exhibit significantly superior photovoltaic performance, achieving a photoconversion efficiency of approximately 12.5%, compared to $\sim 3.8\%$ for CsPbBr_3 based devices. This enhancement is primarily attributed to the narrower bandgap, broader absorption spectrum, and longer carrier lifetime ($\sim 130\text{ ns}$) of CsPbI_3 nanocrystals, which facilitate efficient light harvesting and charge carrier separation (Chapter-2). To further improve the structural stability of CsPbI_3 nanocrystals, a cation doping strategy was employed by incorporating Cu^{2+} ions into the Pb^{2+} lattice sites. Systematic variation of doping concentration revealed that an optimal Cu-doping level ($\sim 5.6\%$) leads to a complete phase transformation from a mixed orthorhombic-cubic structure to a stable cubic α -phase. This transformation is accompanied by a significant enhancement in photoluminescence quantum yield (PLQY), exceeding 80%, along with prolonged carrier lifetime and improved environmental stability. Density functional theory (DFT) calculations provide further insights into the stabilization mechanism, indicating that Cu incorporation leads to charge redistribution, increased bond strength, and reduced formation energy, thereby minimizing structural distortions and suppressing phase transitions (chapter-3). In addition to doping, ligand engineering has been explored as an effective strategy for tuning surface chemistry and improving optical properties. Anion exchange using

n-octylammonium iodide (NOAI) was employed to convert CsPbBr₃ nanocrystals into mixed halide CsPbBr_{3-x}I_x systems, enabling tunable emission across the visible spectrum. Advanced STEM HAADF characterization techniques revealed the presence of Ruddlesden-Popper (RP) faults and grain boundary interfaces within the nanocrystals. Interestingly, these planar defects were found to enhance carrier confinement and facilitate radiative recombination without introducing deep trap states. As a result, a substantial enhancement in electroluminescence intensity (~79%) and improved device performance in flexible LEDs were achieved (chapter-4). Furthermore, a novel post-synthetic ligand-assisted revival strategy was developed to restore the optical properties of degraded CsPbI₃ nanocrystals. Trioctylphosphine oxide (TOPO), a strong Lewis base ligand, was introduced to passivate surface defects and reconstruct the perovskite lattice through strong Pb-O coordination interactions. This treatment effectively recovered the photoluminescence quantum yield from approximately 20% in aged samples to nearly 82%, while also stabilizing the nanocrystal structure over extended periods under ambient conditions. Spectroscopic and structural analyses confirmed that TOPO not only passivated defect states but also facilitated surface reconstruction and morphological transformation, thereby significantly enhancing both stability and optical performance (chapter-5). Overall, the study in this thesis provides a comprehensive understanding of the interplay between structure, surface chemistry, and optoelectronic properties in CsPbX₃ perovskite nanocrystals. By integrating doping strategies, ligand engineering, defect modulation, and revival mechanisms, this work presents effective and scalable approaches for overcoming stability challenges with improved device performance. The findings would contribute to the advancement of perovskite nanocrystals toward practical applications in high-efficiency and stable optoelectronic devices.

Keywords: *Lead halide perovskite nanocrystals, Solar cells, Photoluminescence quantum yield, Ruddlesden-popper faults, Light emitting devices, Density functional theory.*