Stable Perovskite Core-Shell Nanocrystals as Down-Converting Phosphors for Solid State Lighting

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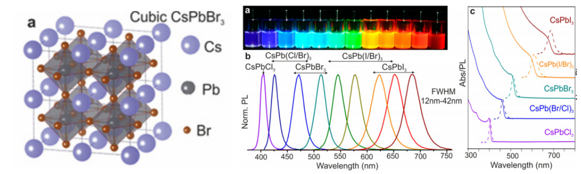
Introduction

- **Cesium-based Perovskite Nanocrystals (NCs)**

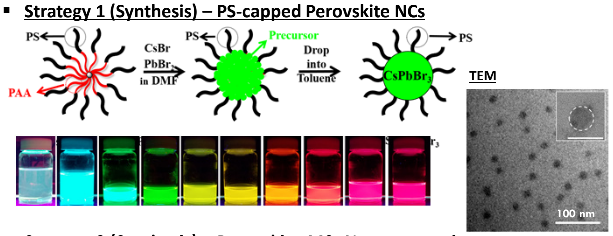


- Cesium-based all inorganic perovskite nanocrystals have bandgap energies through the entire visible spectrum (410-700nm), narrow FWHM (12-42nm), excellent quantum yield (QY, 50-90%), and short radiative lifetimes (1-29 ns).[1]
- The bandgap is easily tunable by either changing the halide composition between chlorine, bromine, and iodine or by controlling the size of the nanocrystals or quantum dots (QDs).[1]
- Potential applications are in LEDs, X-ray Detectors, Lasers, etc.
- HOWEVER, long term stability is currently the major problem.
  - Compositional Mixing
  - Colloidal Aggregation
  - Thermal Degradation
  - Humidity Deterioration
  - Phase Instability

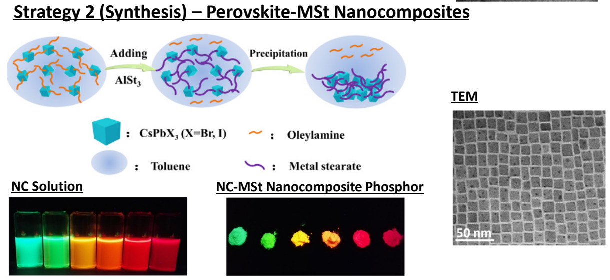
Motivation & Objectives

- Improve stability of colloidal NCs by synthesizing NCs inside a unimolecular star-like block copolymer nanoreactor or impregnating pre-synthesized NCs in metal stearate.
- Utilize permanently tethered PS chains on the $CsPbBr_3$ surface to improve colloidal stability (prevent aggregation) in any solvent that dissolves PS.
- Form a protective shell layer around the $CsPbBr_3$ surface that can block penetration of water or other solvents that will break the perovskite crystal structure.
- Embed NCs in a matrix to improve water, composition, and phase stability.

- **Strategy 1 (Synthesis) – PS-capped Perovskite NCs**

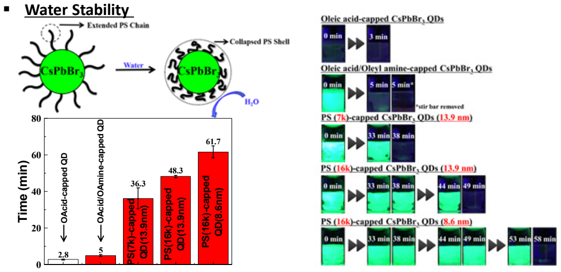


- **Strategy 2 (Synthesis) – Perovskite-MSt Nanocomposites**



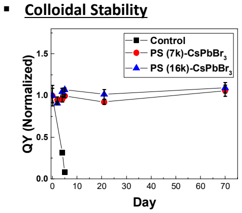
Results & Discussion

- **Stability Enhancements for Strategy 1**
  - **Water Stability**

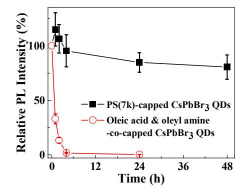


- Schematic represents the polystyrene shell collapse when exposed to water, thus forming a dense protective shell around the perovskite NCs.
- Star-like PAA-*b*-PS nanoreactors with same inner block PAA length but different outer block PS length (7k & 16k) was used to investigate the effectiveness of the PS shell in protecting the NC.
- PS-$CsPbBr_3$ NCs were photoluminescent for up to 20 times longer compared to conventional $CsPbBr_3$ NCs with linear ligands.

  - **Colloidal Stability**

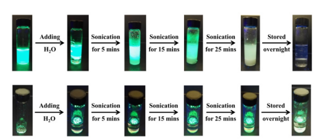


  - **Thermal Stability**

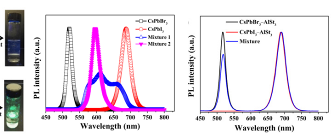


- Conventional $CsPbBr_3$ NCs with linear ligands showed drastic decay under ambient conditions due to colloidal aggregation. (>90% PL Decay in 5 days)
- PS-$CsPbBr_3$ NCs were stable under ambient conditions for more than 2 months. (No PL Decay in 70 days; No PL Shift in 70 days; No Change in FWHM in 70 days)
- PS-$CsPbBr_3$ NCs showed 85% retention in PL at RT after storage at 80°C for 48 h while conventional perovskite NCs completely lost PL during this time period.

- **Stability Enhancements for Strategy 2**
  - **Water Stability**



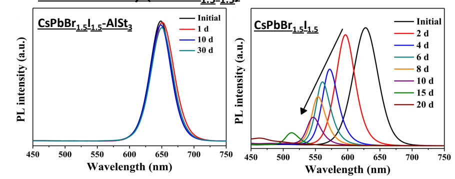
  - **Compositional Stability**



- $CsPbBr_3$-MSt nanocomposites were photoluminescent even after directly exposing to water and sonicating for 25 mins while the $CsPbBr_3$ NCs alone completely lost PL.
- $CsPbBr_3$-MSt nanocomposites did not undergo any compositional mixing and maintained their distinct PL wavelengths even after 24 h of mixing while the NCs not embedded in MSt matrix quickly underwent compositional mixing in just 5 minutes.

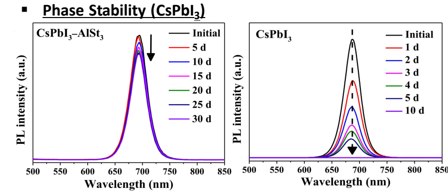
Results & Discussion

- **Stability Enhancements for Strategy 2 (cont.)**
  - **Phase Stability ($CsPbBr_{1.5}I_{1.5}$)**



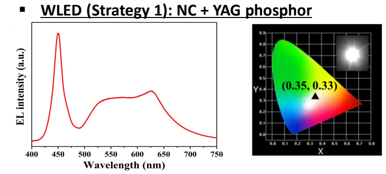
- Phase Segregation Stability of $CsPbBr_{1.5}I_{1.5}$ NCs was greatly improved after embedding the NCs in MSt.

  - **Phase Stability ($CsPbI_3$)**



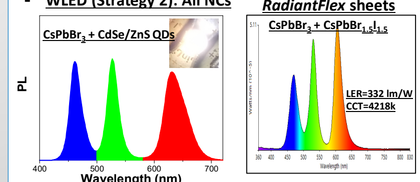
- Phase Stability of $CsPbI_3$ NCs was greatly improved after embedding the NCs in MSt. (85% retention in PL intensity)

- **WLED and *RadiantFlex* sheets Application**
  - **WLED (Strategy 1): NC + YAG phosphor**



- YAG:Ce^{3+} / $CsPbBr_{1.5}I_{1.5}$ NCs-MSt nanocomposites were used to fabricate white light LED.
- Proof of principle demonstration for WLED (CRI = 89.9, CCT = 4588K).

  - **WLED (Strategy 2): All NCs**



- PS-$CsPbBr_3$ NCs and CdSe/ZnS QDs were used to fabricate WLED.
- 116% of NTSC Color Gamut & 163% of sRGB Color Gamut.
- RadiantFlex sheets prepared with perovskite NC-MSt nanocomposites

Conclusions

- Perovskite NCs with PLQY up to 81% and green emission bandwidth as narrow as 17.7 nm, *RadiantFlex* sheets with LER up to 332 lm/W prepared
- PS-$CsPbBr_3$ NCs & $CsPbX_3$-MSt nanocomposites were both much more stable compared to conventional $CsPbBr_3$ NCs when exposed to water.
- PS-$CsPbBr_3$ NCs displayed greatly enhanced thermal stability in solution as well as in a polymer matrix compared to conventional $CsPbBr_3$ NCs.
- $CsPbX_3$-MSt nanocomposites showed great enhancements in compositional as well phase stability compared to conventional $CsPbX_3$ NCs.

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References

1. Protesescu et al. *Nano Letters* 2015, 15, 3692.

Acknowledgement

This work was supported by U.S. DOE-STTR DE-SC0018611