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Improving the Stability of Manganese-Substituted Cs(Pb/Mn)Br3 Inorganic Perovskite Quantum Dots Through Silica-Coating

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Room-Temperature Synthesis of Manganese-Doped Silica-Coated $CsPbBr_3$ Inorganic Perovskite Quantum Dots

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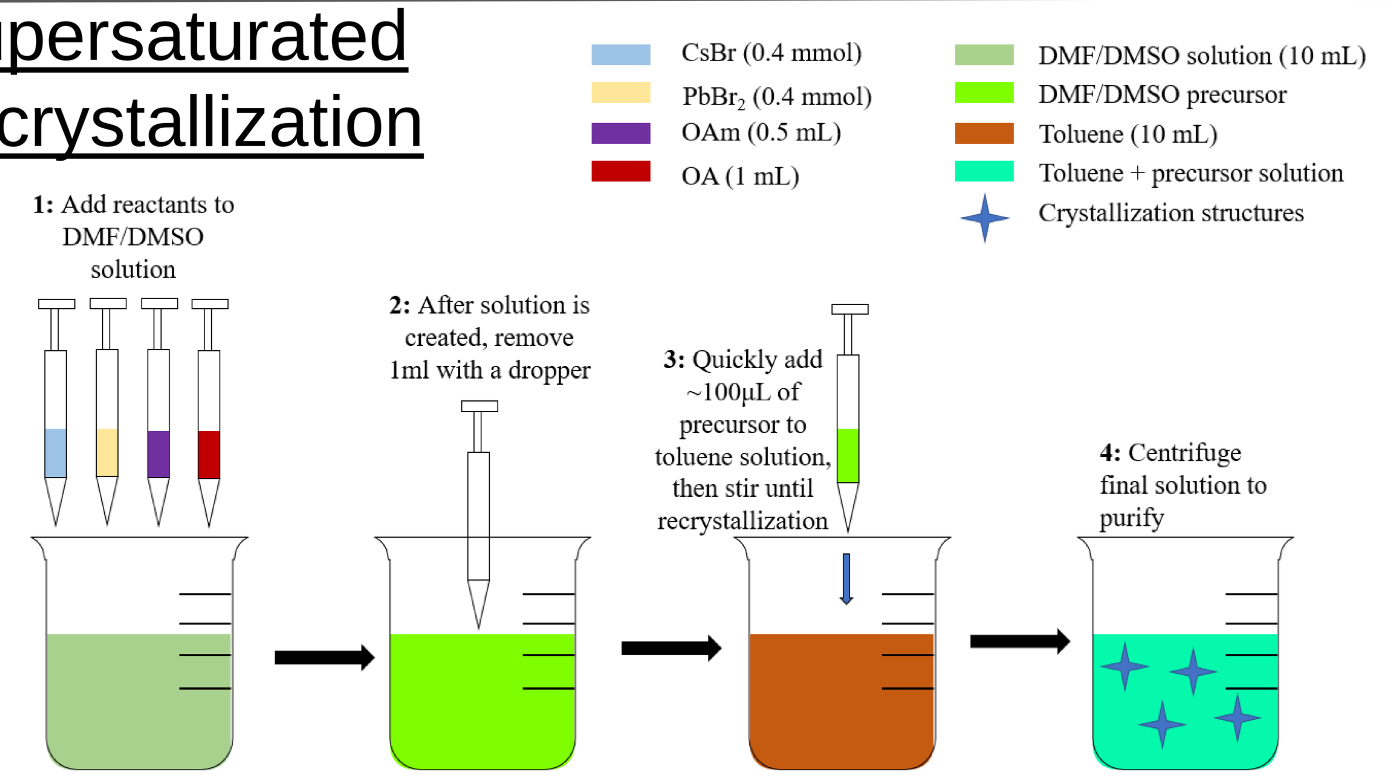
Introduction

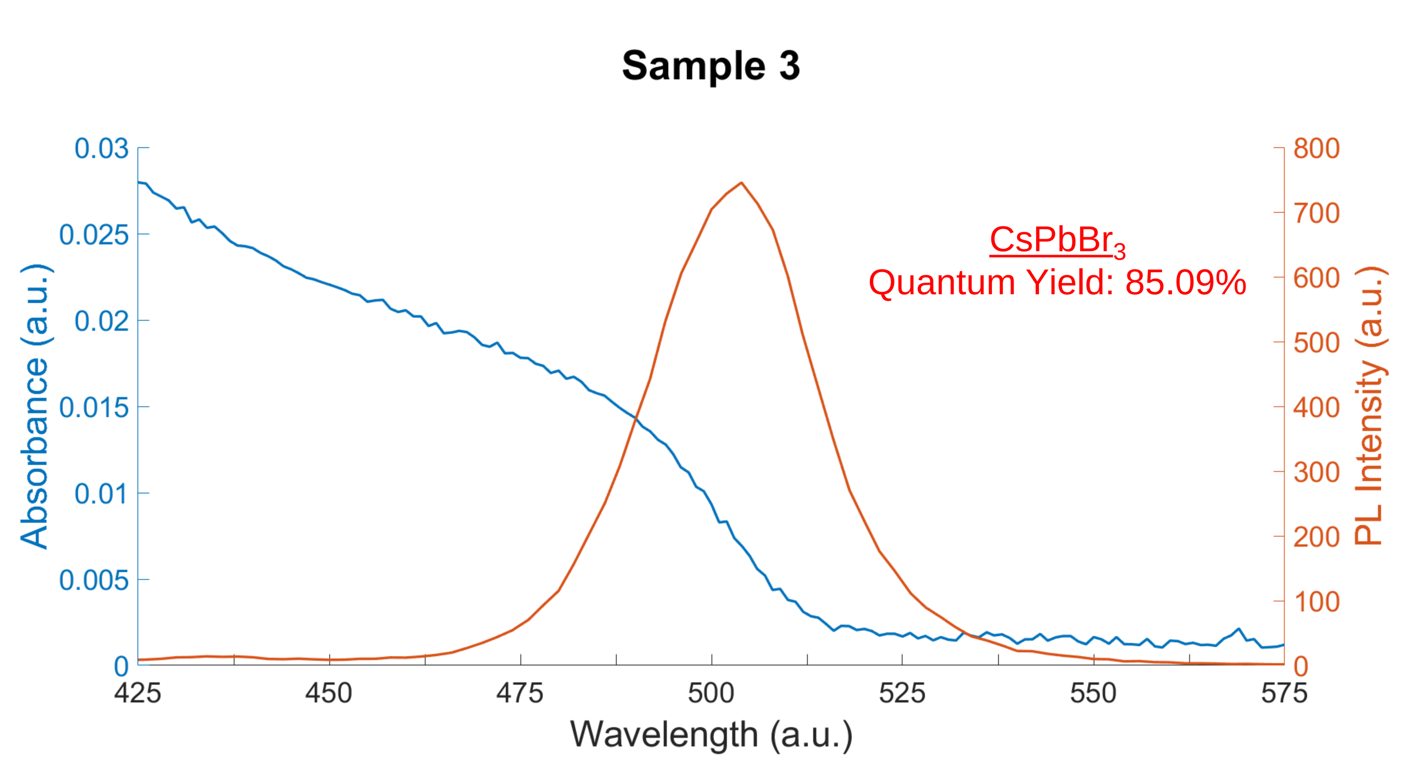
Inorganic perovskite quantum dots (IPQDs) are a unique type of nanocrystal. They are roughly 10nm in size, which causes electron movement to be confined to discrete energy levels. This is known as the quantum confinement effect, which allows these specific energy levels to be tuned depending on the size of the nanocrystal. These tuned energy levels can be used to have the IPQD absorb and emit photons of light at a specific wavelength of light. By having a QD which can absorb and emit at a specific wavelength, you can manufacture QDs which can be used in many optoelectronic devices, such as solar panels and display screens. The efficiency of a QD is measured as the ratio of emitted photons to absorbed photons, better known as quantum yield (QY). Our research was dedicated to improving current drawbacks in IPQDs while maintaining their high QY. Currently IPQDs are unviable in many applications due to the toxicity of lead in them, and their low moisture stability. To fix these issues, we present IPQDs with reduced lead through manganese substitution, and high moisture stability via silica shell coating.

Supersaturated Recrystallization



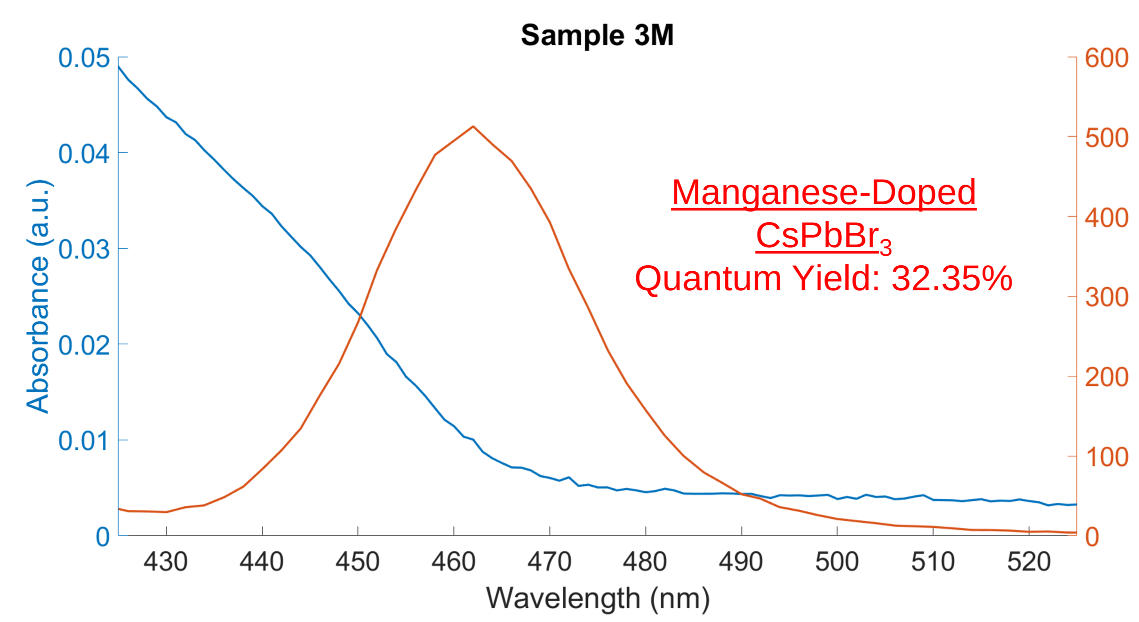
In SSR components are prepared at room temperature and added to solution in the specified order. Stirring of the final two mixtures prompts color change as well as formation of IPQDs. Newer and simpler method of fabrication than hot injection (HI). Requires only one beaker and no need to heat the reaction. SSR can be completed in large quantities, where HI can only be done in small amounts. IPQDs created using SSR have a lower PLQY on average when compared to IPQDs fabricated with HI.

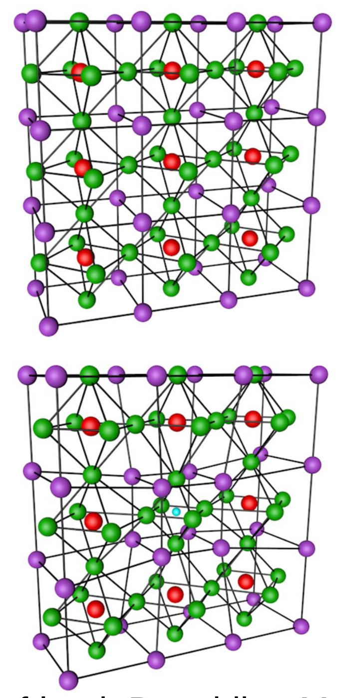
Optical Properties of Synthesized $CsPbBr_3$ Quantum Dots



Analysis: We successfully synthesized $CsPbBr_3$ quantum dots with quantum yields as high as 85.09%. The stability of the samples varied with lifetimes ranging from a few hours to a few months. The successful synthesis of $CsPbBr_3$ quantum dots through the simpler and less dangerous supersaturated recrystallization method shows the viability of this method for future use.

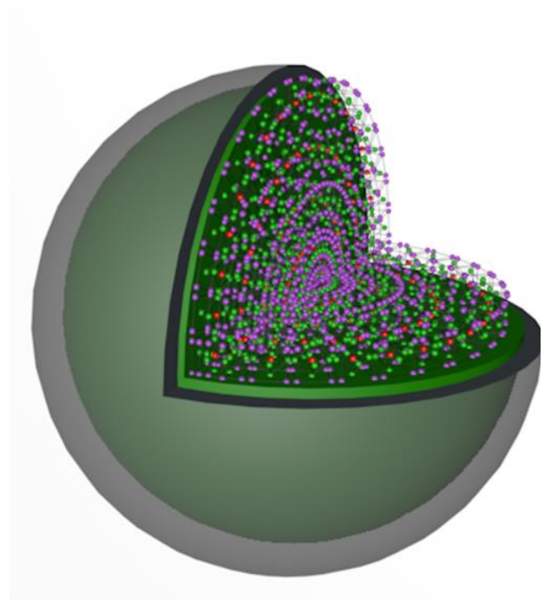
Manganese-Doped $CsPbBr_3$ Quantum Dots

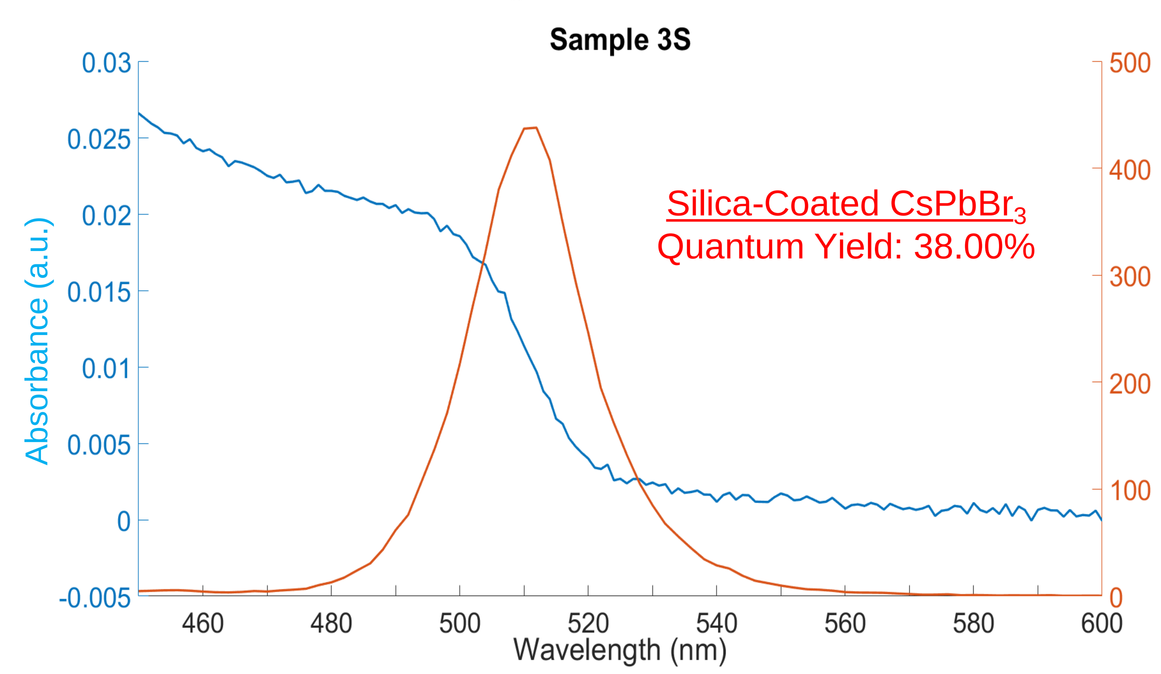




Analysis: Current IPQDs have reduced commercial viability due to the use of lead. By adding MnCl during the synthesis of our IPQDs we were able to reduce the lead content through Mn-doping. Our synthesized Mn-doped IPQDs showed lower photoluminescent areas when compared to our non-substituted IPQDs, but had a higher absorbance. This gave our Mn-doped IPQDs a lower overall quantum yield of 32.35%, confirming our hypothesis.

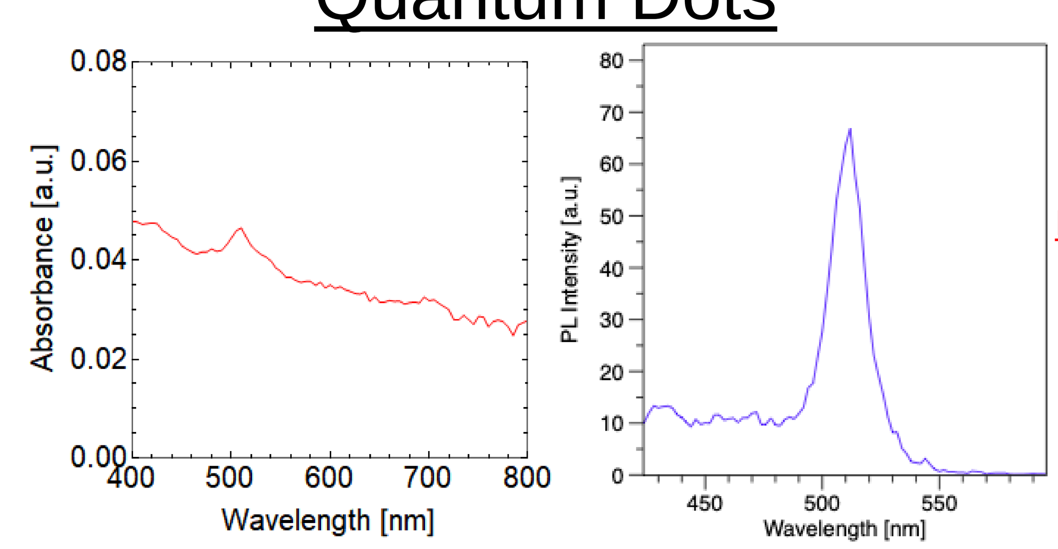
Silica-Coated $CsPbBr_3$ Quantum Dots





Analysis: To improve the stability of our IPQDs, we coated them with a silica shell (SiO_2). The SiO_2 shell gave our IPQD a QY of 38%. We believe that a shell was successfully grown onto the IPQDs due to their ability to fluoresce in water. Their short lifetime in water suggests that the quantum dots were only partially coated with a shell. Our synthesis of water-soluble perovskites shows the importance of shell growth in quantum dot photostability.

Manganese-Doped Silica-Coated $CsPbBr_3$ Quantum Dots



Manganese-Doped Silica-Coated $CsPbBr_3$
Quantum Yield: 4.7%

Analysis: Our previously discussed Mn-doped IPQDs were stirred with TMOS for 48 hours to allow a silica shell to grow. The addition of a silica shell had little effect on the photoluminescent area of our IPQDs and a similarly negligible effect on the absorbance. Our Mn-doped silica coated IPQDs had a quantum yield of 4.7% quantum yield. This sharp decrease in quantum yield was most likely due to the use of DMSO in the IPQD precursor. Although quantum yield was not increased, water stability significantly increased, allowing our IPQDs to successfully disperse in water.

IPQD Fluorescence

Analysis: The above pictures show the different fluorescent emissions we achieved through our IPQD synthesis. We were able to achieve broad blue-green fluorescent emissions in the range of 400-550nm. Our synthesized IPQDs all contained bromine as their halide group, limiting their emissions into this blue-green range. In the future we plan on fabricating IPQDs with different halide groups, such as chlorine and iodide, to achieve full visible spectra emissions.

Conclusions and Future Work

Sample 1 $CsPbBr_3$	74.49
Sample1A $Cs(Mn/Pb)Br_3$	28.20
Sample 1S Silica Coated $CsPbBr_3$	75.70
Sample 2 $CsPbBr_3$	52.13
Sample 2A $Cs(Mn/Pb)Br_3$	42.93
Sample 3 $CsPbBr_3$	85.09
Sample 3M $Cs(Mn/Pb)Br_3$	32.36
Sample 3S Silica Coated $CsPbBr_3$	38.00

Table of Quantum Yields of Synthesized IPQD Samples

Conclusions

- $CsPbBr_3$ IPQDs can be successfully synthesized with the Supersaturated Recrystallization method
- Substitution of lead with manganese led to a decrease in quantum yield and photostability
- Silica coating reduced the quantum yield of $CsPbBr_3$, possibly due to an incomplete shelling
- Silica coating improved the photostability of the $CsPbBr_3$ IPQDs as shown by their ability to fluoresce in water

Future Work

- Further characterization of $CsPbBr_3$ IPQDs with TEM and XRD
- Synthesis of $CsPbCl_3$ and $CsPbI_3$ IPQDs
- Lead substitution with tin, aluminum, and antimony
- Long-term photostability of $CsPbBr_3$ IPQDs vs Silica-coated $CsPbBr_3$ IPQDs
- Comparison of SSR with Hot Injection Synthesis Method

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