

## IN SITU TRANSIENT ABSORPTION SPECTROSCOPY OF ORGANOMETAL HALIDE PEROVSKITE NANOPARTICLES

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### Abstract

We use syringe filtration to rapidly sample a solvation-mediated synthesis of lead halide perovskite nanocrystals, enabling absorbance and fluorescence measurements during nanocrystal formation. The coupling of rapid sampling with a single-shot transient absorption technique will enable characterization of evolving excited state dynamics during nanocrystal nucleation and growth, aiding our ability to tune reaction parameters to achieve desired photophysics.

### Introduction

Hybrid organic-inorganic lead halide perovskites (LHPs) have attracted significant research interest for their exceptional capabilities in optoelectronic applications. In particular, solution processed colloidal nanocrystals (NCs) of these materials demonstrate high fluorescence quantum yield coupled with an easily tunable emission spectrum, making them excellent candidates for use as light emitters [1,2]. The species of capping ligand used, solvent identity, temperature, and duration of growth all act to modulate the resulting photophysics of the final NC population by altering size distribution, morphology, fluorescence quantum yield, and stability [3]. The emergence of these properties during NC synthesis is poorly understood since spectroscopic measurements are rarely performed on nuclei and nascent NCs in situ during the formation process. While spectroscopies such as absorbance and fluorescence are important characterization tools, a complete understanding of NC photophysics requires the use of more complex time-resolved spectroscopies. Transient absorption (TA) spectroscopy is capable of observing the dynamics of excited species in these materials, but this measurement is typically conducted ex situ on fully grown NCs that are structurally at equilibrium. TA measurements must occur while the NC is growing in order to determine how excited state dynamics evolves during synthesis, but the timescale required for most NC syntheses is shorter than that required for data collection using a typical TA instrument. Additionally, NC synthesis is commonly quenched by centrifuging the reaction mixture for several minutes to remove any remaining solid precursors. The removal of solid precursors is particularly important for optical characterization since these components can scatter light and impede spectroscopic study, but the need for centrifugation precludes in situ measurement. While some measurements of absorbance and fluorescence have been made during NC growth [4,5], time-resolved spectroscopies such as TA are currently restricted to NCs at structural equilibrium or during the significantly slower process of NC degradation [6–9].

We have addressed these hurdles by adopting a room-temperature synthesis that occurs in ambient atmosphere and whose NC nucleation and growth kinetics are rate-limited by solvation equilibria for the precursors. As a result, the kinetics of this reaction are more accommodating to in situ measurements, allowing the evolving electronic structure and excited state dynamics to be monitored during NC formation. Here, we demonstrate the use of syringe filters to quench the

reaction and utilize a homemade spectrometer capable of simultaneously collecting absorbance and fluorescence spectra to observe how methylammonium lead triiodide (MAPbI<sub>3</sub>) NCs grow in solution. In conjunction with a single-shot transient absorption (SSTA) technique that lowers the data collection time to a few seconds [10,11], this rapid sampling method enables the measurement of the excited state dynamics of NCs during synthesis.

### Experimental

MAPbI<sub>3</sub> NCs were synthesized using a previously described ligand-mediated transport synthesis [12,13]. Aliquots of 0.5 mL were periodically withdrawn and filtered through a 0.45  $\mu$ m pore PTFE syringe filter into a 1 mm path length quartz cuvette. This lowers the amount of scatter caused by solid precursor, enabling absorption and fluorescence to be measured. The absorbance and fluorescence of these filtered aliquots were measured immediately following filtration unless otherwise noted. The aliquots extracted after 18 min contained too much solid particulate to pass through a syringe filter. All subsequent aliquots were first centrifuged for 10 s and the resulting supernatant was filtered into the cuvette.

An arc lamp and 405 nm laser diode were focused to non-overlapping spots on the cuvette for simultaneous absorbance and fluorescence measurements, respectively, illustrated in Figure 1. Transmitted and emitted light were carried by optical fibers to separate Ocean Optics spectrometers.

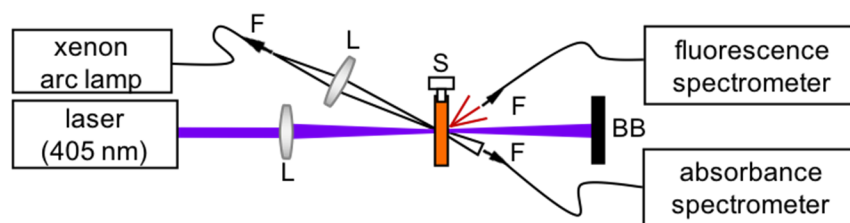


Figure 1. Homebuilt spectrometer used to simultaneously record absorbance and fluorescence of sample (S). Apparatus includes lenses (L), fibers (F), beam block (BB).

### Results & Discussion

Absorbance and fluorescence measurements were collected from 23 aliquots taken at discrete time points during NC synthesis. The evolution of absorbance and fluorescence spectra at selected intervals during the reaction are shown in Figure 2a and 2b, respectively. Initial samples from the reaction mixture exhibit little absorbance and fluorescence until the critical nucleation concentration of precursors is reached by 5 min of reaction time, when a broad, weak feature begins to appear from 600 to 650 nm in the emission spectra. At this stage of the reaction fluorescence is detectable and growing, but absorbance continues to be negligible until the 7 min mark, where a sudden and rapid increase in both absorbance and fluorescence is observed over the subsequent 10 minutes. A sharp feature at 550 nm in the absorbance spectra that grows in by 7 min is consistent with the excitonic band edge of quantum-confined NCs and this excitonic peak continues to gain intensity as the reaction progresses.

Changes in the fluorescence over this same period are less obvious. Early aliquots exhibit features at 600 nm and 636 nm that persist until 10 min, after which the fluorescence spectrum begins to lose intensity on the blue edge and the peak at 636 nm becomes the principle feature. After 18 min of NC growth the fluorescence spectrum redshifts and the emission is centered at 647 nm. This happens together with the appearance of a feature in the absorbance spectrum at 630 nm.

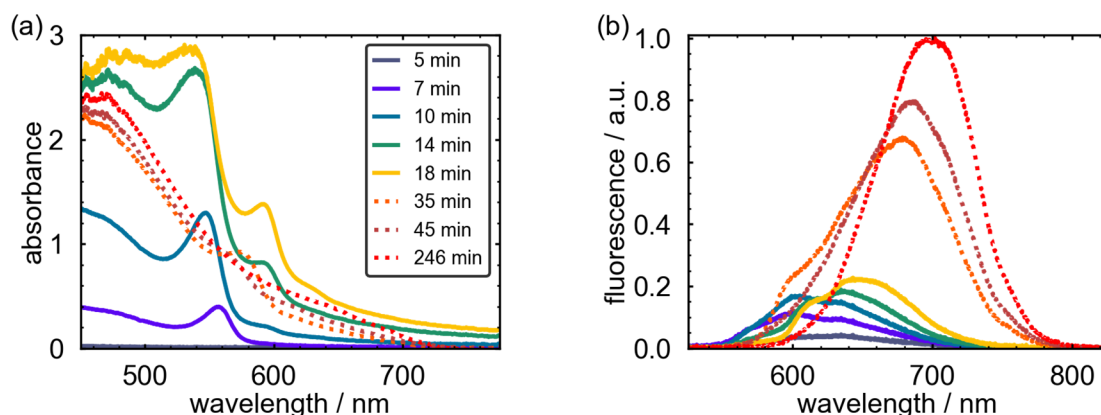


Figure 2. (a) Absorbance and (b) fluorescence measured during synthesis of LHP NCs. Dashed lines indicate the sample was centrifuged before measurement.

Aliquots of the sample from 35 min of reaction time and onward were centrifuged for 10 s prior to filtration to aid in removal of larger solids, which was enough to cause a decrease in the optical density of the samples relative to those that were only filtered. Despite this, the centrifuged samples show a considerable increase in fluorescence intensity. This is attributed to removal of non-emissive components of the reaction mixture through centrifugation, increasing the percentage of incident light that is absorbed by stable, highly emissive NCs. The excitonic feature near 590 nm weakens at longer reaction times and eventually disappears in fully grown NCs, which exhibit increased absorbance at longer wavelengths. After 4 h of growth the absorbance spectrum no longer includes a sharp excitonic peak, instead only exhibiting a shoulder at 650 nm that is consistent with weakly confined excitons in MAPbI<sub>3</sub>. In this same time period the fluorescence loses the high energy shoulder at 600 nm and proceeds to redshift and narrow, consistent with self-sharpening behavior in classical nanoparticle growth [14].

The presented solvation-mediated synthesis has proved capable of producing MAPbI<sub>3</sub> NCs on timescales permitting investigation with time-resolved spectroscopic techniques. The use of filtration as the quenching step in the synthesis allows utilization of a homebuilt spectrometer to simultaneously measure absorbance and fluorescence during the nucleation and growth of MAPbI<sub>3</sub> NCs. These results open the door to novel SSTA measurements of excited state dynamics in NCs during growth to gain insight into how synthetic methods might be leveraged to control the photophysics of NCs.

## References

1. L. C. Schmidt, A. Pertegás, S. González-Carrero, O. Malinkiewicz, S. Agouram, G. Mínguez Espallargas, H. J. Bolink, R. E. Galian, and J. Pérez-Prieto, "Nontemplate Synthesis of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> Perovskite Nanoparticles," *J. Am. Chem. Soc.* **136**, 850–853 (2014).
2. G. Li, F. W. R. Rivarola, N. J. L. K. Davis, S. Bai, T. C. Jellicoe, F. de la Peña, S. Hou, C. Ducati, F. Gao, R. H. Friend, N. C. Greenham, and Z.-K. Tan, "Highly Efficient Perovskite Nanocrystal Light-Emitting Diodes Enabled by a Universal Crosslinking Method," *Advanced Materials* **28**, 3528–3534 (2016).

3. B. Luo, Y.-C. Pu, S. A. Lindley, Y. Yang, L. Lu, Y. Li, X. Li, and J. Z. Zhang, "Organolead Halide Perovskite Nanocrystals: Branched Capping Ligands Control Crystal Size and Stability," *Angewandte Chemie International Edition* **55**, 8864–8868 (2016).
4. L. Qu, W. W. Yu, and X. Peng, "In Situ Observation of the Nucleation and Growth of CdSe Nanocrystals," *Nano Lett.* **4**, 465–469 (2004).
5. B. Abécassis, F. Testard, O. Spalla, and P. Barboux, "Probing in situ the Nucleation and Growth of Gold Nanoparticles by Small-Angle X-ray Scattering," *Nano Lett.* **7**, 1723–1727 (2007).
6. S. J. Yoon, S. Draguta, J. S. Manser, O. Sharia, W. F. Schneider, M. Kuno, and P. V. Kamat, "Tracking Iodide and Bromide Ion Segregation in Mixed Halide Lead Perovskites during Photoirradiation," *ACS Energy Lett.* **1**, 290–296 (2016).
7. Z. Dang, J. Shamsi, F. Palazon, M. Imran, Q. A. Akkerman, S. Park, G. Bertoni, M. Prato, R. Brescia, and L. Manna, "In Situ Transmission Electron Microscopy Study of Electron Beam-Induced Transformations in Colloidal Cesium Lead Halide Perovskite Nanocrystals," *ACS Nano* **11**, 2124–2132 (2017).
8. S. J. Yoon, M. Kuno, and P. V. Kamat, "Shift Happens. How Halide Ion Defects Influence Photoinduced Segregation in Mixed Halide Perovskites," *ACS Energy Lett.* **2**, 1507–1514 (2017).
9. G. F. Samu, C. Janáky, and P. V. Kamat, "A Victim of Halide Ion Segregation. How Light Soaking Affects Solar Cell Performance of Mixed Halide Lead Perovskites," *ACS Energy Lett.* **2**, 1860–1861 (2017).
10. K. S. Wilson and C. Y. Wong, "Single-shot transient absorption spectroscopy with a 45 ps pump-probe time delay range," *Opt. Lett.*, **43**, 371–374 (2018).
11. K. S. Wilson and C. Y. Wong, "In Situ Measurement of Exciton Dynamics During Thin-Film Formation Using Single-Shot Transient Absorption," *J. Phys. Chem. A* **122**, 6438–6444 (2018).
12. J. C. Sadighian, M. L. Crawford, and C. Y. Wong, "Rapid sampling during synthesis of lead halide perovskite nanocrystals for spectroscopic measurement," *MRS Advances*, <https://doi.org/10.1557/adv.2019.263>.
13. L. Wang, N. E. Williams, E. W. Malachosky, J. P. Otto, D. Hayes, R. E. Wood, P. Guyot-Sionnest, and G. S. Engel, "Scalable Ligand-Mediated Transport Synthesis of Organic–Inorganic Hybrid Perovskite Nanocrystals with Resolved Electronic Structure and Ultrafast Dynamics," *ACS Nano* **11**, 2689–2696 (2017).
14. N. T. K. Thanh, N. Maclean, and S. Mahiddine, "Mechanisms of Nucleation and Growth of Nanoparticles in Solution," *Chem. Rev.* **114**, 7610–7630 (2014).