

# Highly Luminescent Phase-Stable CsPbI<sub>3</sub> Perovskite Quantum Dots Achieving Near 100% Absolute Photoluminescence Quantum Yield and Applications to Solar Cells

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## Introduction

Perovskite quantum dots (QDs) as a new type of colloidal nanocrystals have gained significant attention for both fundamental research and commercial applications owing to their appealing optoelectronic properties and excellent chemical processability. For their wide range of potential applications, synthesizing colloidal QDs with high crystal quality is of crucial importance. However, like most common QD systems, those reported perovskite QDs still suffer from a certain density of trapping defects, giving rise to detrimental non-radiative recombination centers and thus quenching luminescence. In this study, we show that a high room-temperature photoluminescence quantum yield (PL QY) of up to 100% can be obtained in CsPbI<sub>3</sub> perovskite QDs, signifying the achievement of almost complete elimination of the trapping defects. This is realized with our improved synthetic protocol that involves introducing organolead compound trioctylphosphine-PbI<sub>2</sub> (TOP-PbI<sub>2</sub>) as the reactive precursor, which also leads to a significantly improved stability for the resulting CsPbI<sub>3</sub> QD solutions. Ultrafast kinetic analysis with time-resolved transient absorption spectroscopy evidences the negligible electron or hole trapping pathways in our QDs, which explains such a high quantum efficiency. We expect the successful synthesis of the “ideal” perovskite QDs will exert profound influence on their applications to both QD-based light-harvesting and -emitting devices.

## Experimental Method

A mixture of 0.12 g of Cs<sub>2</sub>CO<sub>3</sub>, 0.4 mL of oleic acid (OA), 0.4 mL of oleylamine (OAm), and 12 mL of octadecene (ODE) was loaded into a 50 mL three-neck flask and degassed at 110 °C for 3 h with stirring. It was then heated to 120 °C under nitrogen atmosphere until the solution became clear. The temperature was then set from 100 to 170 °C depending on the desired QD size for the subsequent quick injection of the prepared TOP-PbI<sub>2</sub> solution. About 5 secs after injection, the reaction was quenched by immediate immersion of the flask into an ice bath, after which an equivalent volume of methyl acetate (MeOAc) was added to precipitate the QDs followed by centrifugation at 4,000 rpm for 3 min. The supernatant was discarded and the precipitate was dispersed in hexane.

## Results and Discussion

HRTEM image of the product shows monodisperse cubic-shaped QDs with high crystallinity. XPS spectra taken of the Cs, Pb, and I regions for TOP-QDs show peak signals at 723.9, 138.5, and 619.5 eV, which can be well assigned to Cs(I), Pb(II), and I (I). XRD patterns of the resulting QDs can be well indexed to the bulk cubic CsPbI<sub>3</sub>.<sup>1</sup> Urbach energies were derived from absorption spectra of TOP-CsPbI<sub>3</sub> QDs, varying from ~18 to 19 meV, while for traditional QDs, this value is around 30 meV, indicating TOP-QDs have a lower level of electronic disorder and/or defect density.

Very encouragingly, twice-washed (by MeOAc) QDs in all sizes prepared from TOP route exhibit the best-so-far QYs of up to near 100%, higher than that of the traditional route-produced ones with 78-84%. This behavior, indicative

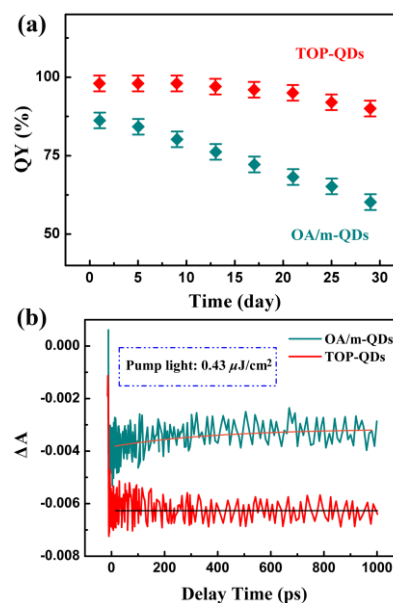


Figure 1. (a) Stability of PL QY of TOP-QDs and traditional one. (b) Comparison of TA response of the two kinds of QDs.

of the absence of non-radiative pathways within the TOP-QDs, is very unusual and rarely observed, even in those traditional high-quality QDs such as CuInS<sub>2</sub> and CdS/Se QDs employing those advanced core/shell passivation techniques. In addition, TOP-CsPbI<sub>3</sub> QDs yield stable QY of 100% for the first 9 days and retain ~85% of its initial value after storage for 1 month. In contrast, traditional QDs show a decreased QY from the initial 86% to 60% after 30 days storage, which in turn suggests a better chemical stability of the resulting TOP-QDs. We couldn't fit the TA curve of TOP-QDs using the same exponential function because no decay can be resolved in the initial 1 ns time scale, which in turn confirms the negligible electron or hole trapping pathways in these TOP-QDs. In order to gain more insight into the fundamental physics behind these appealing optical properties, we therefore monitored the ultrafast exciton relaxation dynamics through transient absorption (TA) spectrum measurements. TA responses of the traditional QDs measured under a low pump light intensity show a slow single-exponential decay in 1 ns time scale with a background signal  $y_0$ . Decay of the photo-excited excitons suggests the presence of recombination pathway due to defects or surface trap states in traditional QDs. However, we couldn't fit the TA curve of TOP-QDs using the same exponential function because no decay can be resolved in the initial 1 ns time scale, which in turn confirms the negligible electron or hole trapping pathways in these TOP-QDs. Solar cells based on these high-quality perovskite QDs exhibit power conversion efficiency of 9%, showing great promise for practical application.

## References

1. Swarnkar, A. *et al.*, *Science* 2016, 354, 92-95.