Full paper

Perovskite quantum dots integrated in large-area luminescent solar concentrators

Haiguang Zhao\textsuperscript{a,1,*}, Yufeng Zhou\textsuperscript{a,1}, Daniele Benetti\textsuperscript{a}, Dongling Ma\textsuperscript{a}, Federico Rosei\textsuperscript{a,b,*}

\textsuperscript{a} INRS Centre for Energy, Materials and Telecommunications, 1650 Boulevard Lionel-Boulet, Varennes, Québec J3X 1S2, Canada
\textsuperscript{b} Institute of Fundamental and Frontier Science, University of Electronic Science and Technology of China, Chengdu 610054, PR China

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\textbf{ABSTRACT}

Luminescent solar concentrators (LSCs) are considered a promising technology to reduce the cost of electricity by decreasing the use of expensive photovoltaic materials, such as single-crystal silicon. In addition, LSCs are suitable for applications in building-integrated photovoltaics. Inorganic perovskite quantum dots (QDs) are promising candidates as absorbers/emitters in LSCs, due to their excellent optical properties including size/chemical-composition dependent absorption/emission spectrum, high absorption coefficient, high quantum yield and good stability. However, due to the large overlap between their absorption and emission spectra, it is still very challenging to fabricate large-area high-efficiency LSCs using perovskite QDs. Here we report the synthesis of mixed-halide perovskite CsPb(BrxI\textsubscript{1−x})\textsubscript{3} QDs with small overlap of absorption and emission spectra, high quantum yield (over 60%) and absorption spectrum ranging from 300 to 650 nm. We use these QDs to build semi-transparent large-area LSCs that exhibit an external optical efficiency of 2% with a geometrical gain factor of 45 (9 cm in length). To date, these represent the brightest and most efficient solution-processed perovskite QDs based LSCs compared to LSCs based on perovskite thin films. The LSCs exhibit long term air stability without any noticeable variation in photoluminescence and lifetime under 4 W UV light illumination for over four hours.

\textbf{1. Introduction}

Solar technologies represent a promising opportunity towards addressing the increasing demand for clean and renewable energy [1–11]. Every hour, radiation impinging from the sun would be sufficient to power the whole planet for one year [12]. However, the cost of the electricity generated by photovoltaic (PV) devices is still quite high. Luminescent solar concentrators (LSCs) are viewed as a promising technology to reduce the cost of electricity by decreasing the use of expensive PV materials, such as single-crystal silicon [13–17]. In addition, LSCs may be used in building-integrated PV applications, such as transparent or semi-transparent solar windows [13,16,17].

They can be made flexible and they are lightweight, compared to commercial silicon or other PV panels [16,18]. A typical LSC consists of a plastic optical waveguide embedded with highly emissive fluorophores [16]. Following absorption of sunlight, fluorophores re-emit photons at a lower energy by down-conversion and these photons are guided towards the PV devices positioned at their edges by total internal reflection (Fig. 1a) [16]. To date, various kinds of fluorophores, such as organic dyes/polymers and inorganic semiconducting nano-crystals have been explored for LSC applications [14–15,19–24]. Among them, quantum dots (QDs) may be singled out due to their multiple advantages, including high quantum yield (QY), size-tunable absorption/emission spectra and better chemical/photostability compared to traditional organic dyes/polymers [14,19–23,25–27].

However, LSCs fabricated using colloidal inorganic QDs still face the following major challenges related to energy loss: i) re-emission because the QY is typically below 100%; ii) re-absorption caused by the overlap between the absorption and emission spectra of the QDs [14,19–21]. Thus the key requisite in terms of optical properties of the fluorophores in high efficiency large-scale LSCs are minimal absorption and emission spectral overlap and a high QY [14,19–21]. Strategies to prevent the reabsorption energy loss in QDs-based LSCs typically include using ions doped QDs and core/shell structured QDs [19–21,28]. Visible emitting QDs including CdSe/CdS [29], CdSe/CdPbS [22], and CdSe/CdZnS QDs [18] exhibit a large Stokes shift (defined as the difference between the positions of the band maxima of absorption and emission spectra) over 400 meV and a QY of 40–70%, leading to a photon conversion efficiency (PCE, the ratio between re-emitted photons reaching the edge of a LSC over incident photons, also

\textsuperscript{*}Corresponding authors.
E-mail addresses: zhaoh@emt.inrs.ca (H. Zhao), rosei@emt.inrs.ca (F. Rosei).
\textsuperscript{1}H. Zhao and Y. Zhou contributed equally to this work.

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known as external optical efficiency) of 1% in CdSe/CdS QDs (LSC dimensions: 21.5×1.3×0.5 cm³) [29] and 1.15% in CdSe/CdPbS QDs (LSC dimensions: 9×1.3×0.2 cm³) [22] for large-area LSCs with a geometrical gain factor (\(G\), defined as the ratio of the area of the top of the LSC and the edge of the LSC coupled with PV cells) over 40 [18,23,29]. However, these visible emitting QDs suffer from incomplete coverage of the solar spectrum due to the large band gap of the absorber material (CdS, 2.5 eV; ZnSe, 2.7 eV) [18,19,21,22,29]. For example, in Mn²⁺-doped ZnSe/ZnS QDs [21], absorption wavelengths are below 450 nm, and in the core/thick-shell CdSe/CdS QDs [29], absorption wavelengths are below 500 nm. Near infrared emitting core/shell QDs such as PbS/CdS [17] and CuInSe₂/ZnS QDs [23] with a typical QY of 40–50% have also been used as emitters for LSCs, while the maximum PCE is still low (~1%) for large-area LSCs with a G over 40 because of the reabsorption energy loss [30]. Very recently, Meinardi et al. showed an external optical efficiency of 2.8% for silicon QDs based LSCs with a G of ~12 (LSC dimensions: 12×12×0.26 cm³). In this system, the as-synthesized silicon QDs are not stable under light and further post-treatment with a 100 W mercury vapor lamp in excess of 12 h was required to improve their photostability [31].

Recently, colloidal hybrid organic-inorganic and inorganic perovskite QDs have been synthesized and used as building blocks in a variety of devices [32–39]. Among various kinds of perovskite QDs, inorganic CsPbX₃ (X=Cl, Br, I) QDs have been widely studied for optoelectronic applications in view of their size/composition dependent absorption and emission spectra, wide absorption spectrum, high brightness with a QY up to 90%, narrow emission linewidth, easy solution phase synthesis and good photostability [32, 33, 37, 39]. Inorganic perovskite QDs may represent a new promising candidate for efficient LSCs.

Here we demonstrate the application of mixed-halide CsPb(BrₓI₁₋ₓ)₃ perovskite QDs as highly emissive fluorophores in high performance large-area LSCs. Specifically, we synthesized CsPb(BrₓI₁₋ₓ)₃ perovskite QDs via a hot-injection approach and incorporated them into poly(lauryl methacrylate-dimethacrylate) (PLMA-EGDA) polymer matrix, resulting in a semitransparent composite with the absorption spectrum ranging from 300 to 650 nm. The prototype LSC based on the perovskite CsPb(BrₓI₁₋ₓ)₃ QDs exhibited an external optical efficiency of 2% with a G of 45.

### 2. Results and discussion

#### 2.1. Synthesis and structure of perovskite QDs

A hot injection synthetic method was used to synthesize colloidal perovskite QDs according to procedures found in the literature [34,39]. Mixed-halide perovskites of CsPb(BrₓI₁₋ₓ)₃ can be readily produced by combining appropriate ratios of PbBr₂/PbI₂ salts. All QDs were synthesized using identical reaction conditions, such as reaction temperature (160 °C) and reaction time (5 s) except for the molar ratio of PbBr₂/PbI₂ salts. Transmission electron microscopy (TEM) was used to characterize sizes and morphologies of as-synthesized QDs (Fig. 2). As shown in Fig. 2a,b,c and S1,S2, mixed-halide CsPb(BrₓI₁₋ₓ)₃ QDs show a typical cubic/cuboidal shape with size between 11 and 15 nm. For example, CsPb(Br₀.₄I₀.₆)₃ QDs exhibit a size of 12.9 ± 1.7 nm (standard deviation, \(\sigma\) < 15%) (Fig. 3c). In a big contrast, CsPbI₃ and CsPbBr₃ QDs show a cubic shape with more uniform size of 7.9 ± 0.3 nm and 8.5 ± 0.3 nm (\(\sigma\) < 7%) , respectively (Fig. 2d,e and S3 a,b). The crystal lattice is clearly visible by high resolution TEM (HRTEM) imaging (Fig. 2b–e). The inset in Fig. 2b displays a micrograph of an individual CsPb(Br₀.₄I₀.₆)₃ QD with a lattice spacing of ~0.597 nm that is well indexed to the (200) plane of the cubic phase, consistently with previous reports [34,39]. The typical cubic structure of mixed-halide perovskite is shown in Fig. 1b. The lattice distances further measured by selected area electron diffraction (SAED) patterns of CsPb(Br₀.₄I₀.₆)₃ (inset image of Fig. 2a) and other perovskite QDs are well indexed to the (200) planes of cubic phase. The measured lattice spacing of (200) decreases with the increase of Br concentration, due to the larger lattice spacing in CsPbI₃ compared to CsPbBr₃ (Table S1). The corresponding energy-dispersive X-ray spectroscopy (EDX) spectrum of an individual CsPb(BrₓI₁₋ₓ)₃ QD with feeding ratio of 40% (Br/(Br+I)) confirms the presence of elemental Cs, Pb, Br/I and 1:1:3 atomic ratio for CsPbX₃ (Fig. S4).

Based on the EDX analysis, with increase of feeding ratio of Br/(Br+I), the real concentration of Br in BrₓI₁₋ₓ increases linearly, indicating the successful control of the chemical composition of mixed-halide perovskite QDs (Fig. 2f) [32, 35, 37].

#### 2.2. Optical properties of perovskite QDs

The absorption and PL spectra of colloidal CsPb(BrₓI₁₋ₓ)₃ QDs with various chemical compositions are reported in Fig. 3a. The absorption spectrum acquired from perovskite QDs can be tuned over the entire window of visible wavelength (300–700 nm) by adjusting their chemical composition (ratio of halides), which allows an efficient capture of solar radiation in this spectral range. The first-excitonic absorption peak shifts to red gradually with the decrease of Br concentration, consistently with the red-shift of the PL peak. Compared to CsPbX₃ (X=Br, I) QDs with PL full width at half maximum (FWHM) of ~17–20 nm, the broadening in the FWHM in mixed-halide perovskite QDs (~35 nm) is due to their lower size uniformity (Fig. S3c). The as-synthesized CsPbI₃ QDs show a typical QY of ~20% ± 2% after purification. This is much lower compared to values of 40–70% reported in the literature [32, 35, 37, 39], which is possibly due to their sensitivity to moisture, since the purification procedure was carried out under normal ambient conditions with average humidity of ~40% [33]. In contrast, mixed-halide QDs exhibit higher QYs compared to CsPbI₃ QDs. When x is over 10%, the QYs of QDs exceed 60%. The CsPbBr₃ QDs show a highest QY of 90%. In addition, mixed-halide QDs or CsPbBr₃ QDs exhibit a very good stability compared to CsPbI₃ QDs. There is no significant QY variation after keeping the CsPb(BrₓI₁₋ₓ)₃ samples at ~10 °C or in a desiccator (20 °C) for 3 months. Compared to CsPbBr₃ QDs or CsPbI₃ QDs, the mixed-halide perovskite CsPb(BrₓI₁₋ₓ)₃ QDs (x=0.1, 0.2, 0.3, 0.4) exhibit a better separation between the absorption and emission spectra (Fig. 3a). This feature has been associated with a Stokes shift as mentioned above. As shown in Fig. 3b, mixed-halide perovskite QDs exhibit a two-fold larger Stokes shift compared to CsPbBr₃ (X=Br, I) QDs, which could reduce the energy loss in large area LSCs. The large Stokes shift has also been found in small-sized CsPbI₃ QDs (~5 nm) synthesized via a non-injection approach [33]. In colloidal QDs, typically a Stokes shift arises from a combination of the effects of band-edge fine-structure splitting, phonon-assisted emission and size polydispersity [40,41].

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**Fig. 1.** Perovskite QDs based LSC. (a) Scheme of a typical LSC configuration. (b) Cubic structure of mixed-halide perovskite QDs of CsPb(BrₓI₁₋ₓ)₃.
larger Stokes shift in mixed-halide QDs may originate from their larger size distribution compared to single perovskite QDs. As shown in Fig. S3, the standard deviation ($\sigma$ ~15%) of mixed-halide QDs is two-fold of that of pure perovskite QDs ($\sigma$ ~7%). The larger size distribution leads to the self-quenching of the PL as high energy photons emitted by smaller QDs may be absorbed by larger QDs with a narrower bandgap [41]. This effect leads to the red-shift of PL peaks and the decrease in QY. Because the absorption peak does not change, the red-shifted PL peak leads to a larger Stokes-shift in mixed halide QDs [41]. This self-PL quenching also leads to a decrease of QY due to the reabsorption energy loss (Fig. 3b) in mixed halide QDs compared to CsPbBr$_3$ QDs. PL decay curves of perovskite QDs with different Br concentration were shown in Fig. 3c,d. The PL lifetime of CsPbBr$_3$ QDs is around 9 ns and that of mixed-halide QDs is in the range of 18–21 ns, which are consistent with the reported values for high-QY perovskite QDs [39]. The PL lifetime of CsPbI$_3$ QDs is around 26 ns which is longer than both mixed-halide QDs and CsPbBr$_3$ QDs, consistent with their lower QYs, which is mainly due to the increase of non-radiative decay rate induced by traps/defects [33,34,39].

2.3. Perovskite QD based LSCs

We now focus on fabricating large-area LSCs using CsPbBr$_3$ and mixed-halide perovskite QDs. We quantify the reabsorption by a parameter of quality factor ($Q_2$, defined as the ratio between the absorption coefficient ($\alpha_2$) at the wavelength $\lambda_2$ of collected light and the absorption coefficient ($\alpha_1$) at the emission peak) as shown in Fig. S5 [28]. This parameter ($Q_2$) is four in CsPb(Br$_{0.5}$I$_{0.5}$)$_3$ QDs, which is four times higher than that of CsPbBr$_3$ QDs ($Q_2$=0.97). This is consistent with the larger Stokes shift in mixed-halide QDs, indicating a small overlap of absorption and emission spectra in mixed halide QDs [28]. The as-synthesized perovskite QDs were dispersed into monomers of lauryl methacrylate and crosslinking agent of ethylene glycol dimethacrylate (wt% of 5:1) and a UV initiator (diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide [22,23,30,31]. Crosslinked poly(lauryl methacrylate) (PLMA) has long side chains that can interact with surface long-chain ligands to prevent agglomeration of the QDs during polymerization [22,23,30,31]. In addition, by carefully controlling the polymerization conditions, such as molar ratio between the monomer and cross-linker, crosslinked PLMA exhibits high optical quality LSCs, such as high-transparency in the visible and near infrared ranges (>95%, better than PMMA) [29,30,31]. The high quality of PLMA with less unconverted monomers has been widely used as a polymer matrix in high efficiency LSCs based on colloidal QDs [22,29,30,31]. After 2-h UV illumination, we fabricated LSCs using various kinds of perovskite QDs. As shown in Fig. 4a, the square large-area LSC (0.2×6×6 cm$^2$) appears semi-transparent in ambient environment, and a clear concentrated red light can be seen from the edges (Fig. 4b), when the top surface of the LSC is partially placed under one sun illumination (100 mW/cm$^2$). Fig. 4c presents a photograph of two overlapping LSCs using CsPbBr$_3$ QDs (green) and CsPb(Br$_{0.5}$I$_{0.5}$)$_3$ (red) QDs under UV illumination, in which both bright green and red emission are clearly visible, indicating the possible fabrication of tandem semi-transparent LSCs using perovskite QDs [42].

LSCs based on mixed-halide perovskite QDs exhibit an absorption...
spectrum in the wavelength range 300–650 nm (Fig. 4d). No significant changes in the PL peak position or FWHM were found for the investigated samples before (in solution) and after embedding the QDs into the polymer matrix (Fig. 4c,d). We estimate the relative QYs of QDs in polymer matrix by considering the variations in lifetime [29,30].

The QY can be expressed as:

\[
QY = \frac{k_{et}}{k_{et} + k_{net}}
\]

where \(k_{et}\) and \(k_{net}\) are the radiative and the non-radiative decay rate, respectively.

The measured lifetime is equal to:

\[
\tau = \frac{1}{k_{et} + k_{net}}
\]

The absence of additional non-radiative decay channels \(k_{net}\) in the CsPb(BrxI\(_{1-x}\))\(_{3}\) QDs/polymer was confirmed by PL decay measurements, which showed identical dynamics for the CsPb(BrxI\(_{1-x}\))\(_{3}\) in toluene and after encapsulation in the polymer (Fig. 3e), indicating that...
the preparation process does not lead to the formation of a significant density of surface-defects/traps \[19,29\]. The polymerization process only affects kinetic of QDs \[29\]. Since the measured lifetime of investigated CsPb(Br_{0.2}I_{0.8})_3 QDs does not change after embedding them in the polymer, we can deduce that the factor (\(k_{\text{em}} + k_{\text{net}}\)) does not change either \[29\]. This is a clear indication that the mixed-halide QDs embedded in the polymer keep almost the same QY as in solution. On the other hand, the lifetime in the CsPbI_3 QDs/polymer largely increases from 25 to 60 ns due to the presence of traps, indicating that the CsPbI_3 QDs are not stable under UV illumination \[43,44\]. These results clearly confirm that the mixed-halide CsPb(Br_{1-x}I_x)_3 QDs present a better photostability compared to CsPbI_3 QDs under high dose UV illumination (~40 W/cm²). The PL does not vary significantly during the further storage of LSCs under ambient condition for 5 months due to the protection of polymer which can protect the QDs from exposure to moisture or oxygen \[3, 23, 35,43,44\].

We further measured the absorption and PL spectra of perovskite QD based LSCs at different optical paths for the mixed-halide CsPb(Br_{1-x}I_x)_3 and CsPbBr_3 QD based LSCs (Fig. 4d and Fig. S6). The overlap between absorption and emission spectra is significantly larger in CsPbBr_3 compared to CsPb(Br_{0.2}I_{0.8})_3. Specifically, the PL signals from the LSC are recorded at a certain distance between the edge and vertically illuminated spot at excitation wavelength of 440 nm (Fig. S7a). We plot the integrated PL area as a function of the optical path \[31\]. The change in the PL signal with respect to PL FWHM and PL peak position can only occur due to spectral distortion because of light reabsorption by the perovskite QDs \[23\]. In our case, by increasing the optical path, the PL spectra of both types of QDs exhibit a red-shift up to 8 nm with a narrowing of the PL FWHM which confirms the energy loss due to light reabsorption (Fig. 4d and Fig. S6). In future work we plan to investigate the mechanisms of energy loss in LSCs \[45\]. The reduced reabsorption loss and high external optical efficiency make mixed-halide perovskite QDs potentially excellent candidates for fabricating large-area high-efficiency LSCs.

Standardization of efficiency measurements in LSCs are still an open issue. For this reason, to allow a fair comparison of our results with previous achievements in the literature, in this study we used the set-up described in Refs. \[22,29,30\] (Fig. S8a). The LSC (dimension: 0.2×1.5×11 cm³) was illuminated perpendicular to its surface by a 1.5 AM global solar simulator (100 mW/cm²). In the photograph (Fig. S8a), a standard silicon solar cell with known external quantum efficiency (Fig. S8b) was coupled with one of the edges of the LSC. Other three edges were coupled by optical mirrors. We also measured the emitted light intensity by coupling a standard power-meter on one of the edges of the LSC. By applying the aforementioned scheme (described in detail in the Methods section), we focus on the calculation of the external optical efficiency (also named as PCE). A common method to estimate \(\eta_{\text{opt}}\) is to couple a PV cell (usually a Silicon solar cell with well-known PV parameters, details in the SI) at the end of the LSC. In this case, \(\eta_{\text{opt}}\) can be calculated as \[16, 22, 30\]:

\[
\eta_{\text{opt}} = \frac{I_{\text{SC}} \cdot A_{PV}}{I_{\text{SC}} \cdot A_{LSC}} = \frac{I_{\text{SC}}}{I_{\text{SC}} \cdot G}
\]

where \(I_{\text{SC}}\) is the short circuit current generated by the cell coupled to the LSC, \(I_{\text{SC}}\) is the short circuit current of the same PV cell under direct
illumination, \( \eta_{\text{PV}} \) is the area of the edge of the LSC (or the active area on the PV cell, if the area is smaller) and \( A_{\text{LSC}} \) is the area of the top of the LSC.

As expected, \( \eta_{\text{PV}} \) of LSCs using CsPb(Br\(_{0.2}\)I\(_{0.8}\)) QDs drops exponentially with the increase of the G factor of the LSCs, which is consistent with our simulation (Fig. 5a).

A maximum external optical efficiency of \( \eta_{\text{opt}} = 2\% \) is achieved with G of 45 (Fig. 5a). Increasing the G factor up to 55 (corresponding to a LSC length of 11 cm) \( \eta_{\text{opt}} \) decreased to \(-1.45\% \) due to reabsorption and scattering loss. The 2\% of \( \eta_{\text{opt}} \) of LSCs using CsPb(Br\(_{0.2}\)I\(_{0.8}\)) QDs is four times higher than that of LSC using CsPbBr\(_3\) QDs (0.5\%) or CsPbI\(_3\) (0.4\%) with the same G factor of 45 and optimal concentration. There is no significant difference in external optical efficiency measured by silicon solar cell or power meter. The low external optical efficiency in single perovskite QDs is due to their large overlap between the absorption and emission spectra. Moreover, the \( \eta_{\text{opt}} \) of 2\% obtained with the mixed-halide perovskite QDs based LSCs is higher than other recent QDs-based LSCs (see Table 1). The organic–inorganic hybrid perovskite thin film, e.g. CH\(_3\)NH\(_3\)PbI\(_3\) [46] and CH\(_3\)NH\(_3\)PbBr\(_3\) [47] have been used as emitters for small-sized LSCs with an external optical efficiency of \(-13\% \) (1.5×1.5×0.01 mm\(^3\)) [46]. However due to the strong overlap between the absorption and PL spectra, it is still very challenging to fabricate large-area LSCs.

In view of the high external optical efficiency obtained at G=45, we further explored the possibility to realize large-area high-efficiency LSCs with perovskite QDs exhibiting higher QY or a higher quality factor. We implemented the analytical model of planar LSCs reported in Ref. [28], (details for simulation are included in the Methods). With a similar formalism, we can accurately fit the results of the external optical efficiency, concentration factor and internal quantum efficiency (IQE) as reported in Fig. 5. The IQE represents the number of photons emitted by the edge of the LSC over the number of photons absorbed by the LSC. We observe the consequence of an increase in the IQE of the CsPb(Br\(_{0.2}\)I\(_{0.8}\)) QDs: increasing the QY up to 75\% (from 60\% of synthesized QDs) the efficiency would increase to 3.6\% at G=45 and 5.9\% at G=10 respectively. An ideal CsPb(Br\(_{0.2}\)I\(_{0.8}\)) QDs, with QY of 1, would have a maximum external optical efficiency of more than 6\% at G=45.

Improving the PL QY from 0.6 to values close to 1 can be very challenging because the as-prepared perovskite QDs should have almost perfect crystal structure without any defects/traps and very narrow size distribution (a−5\%) to avoid any of the self-PL quenching due to the spectral overlap between the luminescence and absorption. Such improvements can potentially be achieved by coating QDs with protective organic or inorganic ligands, forming a core/shell structure and refining reaction conditions to synthesize QDs with very narrow size distribution. Another possible way to increase the external optical efficiency is to increase the QF [28]. Fig. 5b reports simulation results of the effect of increasing QF (and so the Stokes-shift) of the CsPb(Br\(_{0.2}\)I\(_{0.8}\)) QDs on the internal quantum efficiency of the LSC. For example, with a QY=75\% and QF=20 it is possible to achieve the same efficiency at G=45 as in the case of QDs with QY of 100\%. Instead preserving the same QY of synthesized QDs, but with a QF improved to 50, we could be able to maintain an IQE of 40\% with a G of 70, which is comparable to LSCs made with QDs with QY of 1 (G=12.5).

Compared to colloidal perovskite QDs which lack long-term stability due to the sensitivity of the moisture, after encapsulation of perovskite QDs into the polymer matrix, the LSCs exhibit very good stability with respect to photocorrosion. After UV illumination (20 mW/cm\(^2\)) for 14 h, the optical properties of perovskite QDs or mixed halide perovskite QDs based LSCs (PL intensity, PL peak position and PL FWHM) do not show any significant change (Fig. 6a and b). Upon exposure to a high dose of UV illumination (100 mW/ cm\(^2\)), equal to 20 sun illumination [23]), within the first four hours, the PL peak position and PL FWHM of the perovskite QDs do not change significantly compared to their values before and after UV illumination (Fig. 6a and b). Similarly, the PL lifetime of perovskite QDs of both

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**Table 1**

<table>
<thead>
<tr>
<th>LSC</th>
<th>( \eta_{\text{PV}} ) (%)</th>
<th>G factor</th>
<th>LSC dimensions (cm(^2))</th>
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<tr>
<td>CdSe/CdS QDs</td>
<td>1.15</td>
<td>45</td>
<td>9×1.3×0.2(^2)</td>
<td>[22]</td>
</tr>
<tr>
<td>PbS/CdSe QDs</td>
<td>1</td>
<td>10</td>
<td>9×1.3×0.2(^2)</td>
<td>[30]</td>
</tr>
<tr>
<td>CdsS/ZeO (_2) QDs</td>
<td>3.2</td>
<td>10</td>
<td>12×12×0.3(^2)</td>
<td>[23]</td>
</tr>
<tr>
<td>Si QDs</td>
<td>2.86</td>
<td>12</td>
<td>12×12×0.25(^2)</td>
<td>[31]</td>
</tr>
<tr>
<td>CH(_3)NH(_3)PbI(_3) thin film</td>
<td>13</td>
<td>15</td>
<td>1.5×1.5×0.01(^2)</td>
<td>[46]</td>
</tr>
<tr>
<td>Mixed halide perovskite QDs</td>
<td>2</td>
<td>45</td>
<td>9×1.3×0.2(^2)</td>
<td>This</td>
</tr>
</tbody>
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\(^{a}\) The measurement set up is similar to Fig. S8b, one edge was coupled with PV device.

\(^{b}\) One edge of the LSC was coupled with PV device. Other three edges of the LSC were not coupled by optical mirrors.
CsPbBr₃ and CsPb(Br₀.₂I₀.₈)₃ in polymer matrix exhibits similar values after and before UV exposure (Fig. S9a and b). When increasing the illumination time (10 h), the PL intensity still maintains over 90% of its intensity for both bare and mixed halide perovskite QDs based LSCs (Fig. 6). Further UV illumination leads to a decrease in PL intensity, but the PL peak position and PL FWHM do not change significantly. Significant variations in PL FWHM and PL peak position are generally attributed to phase segregation which creates iodide-rich and bromide-rich domains in mixed halide perovskite QDs. Therefore we believe that in our case this phase segregation did not occur [43]. A similar remarkable photostability has been reported for perovskite QD films under continuous pulsed laser excitation in ambient conditions for at least 34 h (corresponding to 1.2×10⁸ laser shots, 12 mJ/cm²) [44]. In addition, there is no significant change regarding the color and external optical efficiency of the LSCs after storing at ambient conditions for more than three months. This indicates better stability compared to LSCs based on perovskite thin films, in which the external optical efficiency drops by 15% after four-week storage [46]. These results indicate that inorganic perovskite QDs based LSCs are very promising for solar energy applications.

As lead is toxic [48], future work should focus on synthesizing lead-free perovskite QDs, such as bismuth halide perovskite QDs (MA₂Bi₂Br₉) [49] and tin halide perovskite QDs (CsSnI₃) [50]. Mixed halide perovskite QDs based on Bi and Sn may present a promising emitter for large-scale LSCs.

3. Conclusions and perspectives

We demonstrated large-area and high-efficiency LSCs based on colloidal CsPb(BrₓI₁₋ₓ)₃ QDs dispersed in a polymer matrix. By tuning the chemical composition of Br/I, we can efficiently enlarge the Stokes shift of QDs, leading to a better separation between the absorption and emission spectra. The as-prepared mixed-halide perovskite QDs exhibit a high QY over 60% with good photostability. Due to their broad absorption and relatively low reabsorption loss, large-area LSCs based on CsPb(BrₓI₁₋ₓ)₃ QDs exhibit an external optical efficiency of 2% (G=45). The LSCs exhibit long term air stability without any noticeable variation in PL intensity and lifetime under 4 W UV light illumination for over four hours. The concept can be applied in near infrared LSCs by tailoring the chemical composition of the perovskites, such as Cs(PbₓSn₁₋ₓ)(BrₓI₁₋ₓ)³ QDs or lead-free CsSn(BrₓI₁₋ₓ)₃. In view of the simple synthesis procedure and excellent optical properties of CsPb(BrₓI₁₋ₓ)₃ QDs, they represent a practical emitter for large-area, high efficiency LSCs and are also promising candidates for other optoelectronic applications, such as light emitting devices, field effect transistors and solar cells.

4. Methods

4.1. Chemicals and materials

Oleic acid (OA, 90%), octadecene (ODE), oleylamine (OLA, 80–90%), Cs₂CO₃ (99%), butanol, lead(II) iodide (PbI₂, 99.999%), lead(II) bromide (PbBr₂, 99.999%), Rhodamine G, laurel methacrylate, ethylene glycol dimethacrylate, (diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, and toluene were purchased from Sigma-Aldrich. All chemicals were used as purchased.

4.2. Synthesis of Cs-oleate [34,39]

A solution of OA (0.6 mL) and Cs₂CO₃ (0.2 g) in 7.5 mL of ODE was stirred and heated to 200 °C until the white powder was completely dissolved. Then the mixture was kept at 130 °C for one hour under vacuum. The temperature of the Cs-oleate mixture was kept at least at 80 °C to avoid precipitation.
4.3. Synthesis of perovskite QDs [34,39]

Perovskite QDs were synthesized by using a hot injection approach. Typically, in a 100 mL round-bottom flask, OA (2 mL), OLA (2 mL), ODE (20 mL) and 290 mg of PbBr2 (or 368 mg PbI2) were degassed at 100 °C for 30 min. The reaction flask was re-stored with N2 and heated to 130 °C for 30 min under vacuum. The temperature was further increased to 160 °C, followed by the rapid injection of 1.8 mL of Cs-oleate solution. The reaction was kept at 160 °C for 5 s and then the solution was rapidly cooled by the water bath. For the synthesis of the mixed-halide perovskite QDs, a mixture of PbBr2/PbI2 with different molar ratios (1:9, 2:8, 3:7, 4:6 and 5:5) was used as halide precursors. Other reaction conditions, such as injection temperature and reaction time are the same with the synthesis of CsPbBr3 or CsPbI3 QDs. Butanol was added, then the suspension was centrifuged and the supernatant was removed. The QDs were then dispersed in toluene for further characterization. The as-prepared QDs are very sensitive to moisture and need to be kept in a desiccator or a refrigerator at −10 °C.

4.4. Device fabrication [22,30]

The LSCs were fabricated by embedding perovskite QDs in the polymer matrix. Perovskite QDs (50 mg) dispersed in toluene were added to a 50 mL flask and the solvent vapor was pumped away. The monomer precursors of lauryl methacrylate and ethylene glycol dimethacrylate (wt% of 5:1) and a UV initiator (diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide) were mixed and sonicated until a colourless solution (3 mL) was obtained. The solution was then transferred into the flask containing the solvent free perovskite QDs. The mixture was homogeneously dispersed by ultrasound treatment, then injected into a mold consisting of two glass slides separated by a flexible silicon rubber spacer of thickness ~2 mm. The mixture was kept under UV illumination (with a wavelength of 400 nm) for 2 h.

4.5. Characterization

TEM characterization of the QDs was carried out using a JEOL 2100F TEM equipped with an EDX spectrometer and SAED. TGA (Q500) was used to identify the concentration of QDs inside the LSCs. Absorption spectra were acquired with a Cary 5000 UV–vis–NIR spectrophotometer (Varian) with a scan speed of 600 nm/min. Fluorescence spectra were acquired with a Fluorolog-3 system (Horiba Jobin Yvon). The PL lifetime of the perovskite QDs in solution and in the polymer matrix was measured using a pulsed laser diode of 440 nm and Time-Correlated Single Photon Counting (TCSPC) mode in the Fluorolog-3 system. QYs of QDs were measured by using Rhodamine 6G as a reference.

The external optical efficiency of the LSCs was measured by using an ABET2000 solar simulator at AM 1.5G (100 mW/cm²) calibrated using a reference Si solar cell. LSCs were prepared with different lengths and their external optical efficiency was tested by illuminating the full area of the LSC, with one edge mounted with a Si solar cell and other three edges and bottom facing commercial mirrors, as illustrated in previous work [22,30]. The Si solar cell used was a commercial model (IXYS KXOB22). Since the total area of the Si cell is larger than the edge area of the LSC, a black tape was used to mark the excessive area of the cell and leave an exposed surface of 0.3 cm² (same as the edge of the LSC). The performance parameters of the cell are as follows: PCE=4.65%, JSC=20.3 mA/cm², VSC=0.51 V, FF=0.45. The current-voltage (I-V) characteristics of the Si solar cell, laterally coupled to the LSC, were measured by a Keysight 2900A SourceMeter, when the LSC was illuminated under simulated sunlight.

4.6. Analytical model for efficiency simulation of LSC with perovskite QDs

Following the formalism developed elsewhere [28], the efficiency of the LSC can be expressed as:

$$\eta_{\text{optical}} = \frac{1.05(1-R)(1-e^{-\alpha d}) \eta_{\text{poly}} \eta_{\text{IR}}}{1+\beta \alpha L(1-\eta_{\text{poly}} \eta_{\text{IR}})}$$

in which $<\alpha_d>$ is the spectrally averaged absorption coefficient, $d$ is the thickness of the LSC, $\eta_{\text{poly}}$ is the estimated QY of the perovskite QDs, fixed to 0.5; $\eta_{\text{IR}}$ is the total internal reflection efficiency of the polymer waveguide that can be estimated to be around 73%; $\beta$ is a numerical value fixed to 1.4 as in Ref. [28], $\alpha_t$ is the absorption coefficient at the wavelength $\lambda_2$, peak of the emitted light; $R$ is the fraction of the incident light reflected by the collecting surface, that can be calculated, considering the normal incidence of the simulated sunlight as:

$$R = \frac{(\eta_{\text{poly}} - n_{\text{air}})^2}{(\eta_{\text{poly}} + n_{\text{air}})^2}$$

where $n$ is the refractive index of polymer or air. With the polymer utilized, $R$ can be estimated to be 3% (Ref. [22]).

To correct the underestimation of the overall efficiency resulting from neglecting effects of reabsorption/reemission within the escape cone, a correction factor of 5% has been introduced.

Because our experimental data on external optical efficiency have been obtained a simulated solar light with non-monochromatic spectrum we used a spectrally averaged absorption coefficient $<\alpha_t>$ defined as:

$$<\alpha_t> = -\frac{1}{d} \int_{\lambda_1}^{\lambda_2} \frac{S_{\text{PL}}(\lambda) \alpha(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} S_{\text{PL}}(\lambda) d\lambda}$$

in which $\lambda_1$ is the wavelength from which the perovskite QDs start to absorb light, $\alpha$ is the absorption coefficient and $S_{\text{PL}}$ is the solar irradiance at 1.5G.

To obtain a better fit of the experimental data, $\alpha_t$ can be replaced by its averaged value $<\alpha_2>$. This allows us to take in account the variation of the absorption coefficient along the emission band. $<\alpha_2>$ can be determined as follows:

$$<\alpha_2> = \frac{\int_{\lambda_1}^{\lambda_2} S_{\text{PL}}(\lambda) \alpha(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} S_{\text{PL}}(\lambda) d\lambda}$$

in which $S_{\text{PL}}(\lambda)$ is the PL emission spectrum.

From (1) it is also able to obtain the internal quantum efficiency as:

$$\text{IQE} = \frac{\eta_{\text{PL}} \eta_{\text{IR}}}{1 + \beta <\alpha_2> L(1-\eta_{\text{poly}} \eta_{\text{IR}})}$$

The concentration factor was also calculated and the detail is included in the Supporting information (Fig. S10).

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References

[18] Haiquang Zhao is a Research Associate of the INRS Centre for Energy, Materials and Telecommunications, Quebec University, Varennes (QC) Canada. He received his MSc degree (2007) from Zhejiang University and PhD degree (2012) from INRS, Quebec University. He is currently a sub-group leader in Prof. Rosei’s group in INRS. His research interests focus on the synthesis of semiconductor materials (including metal oxide, quantum dot and perovskite) for solar energy applications, such as solar cell, luminescent solar concentrator and solar-driven water splitting.
[19] Yufeng Zhou received a Master Degree at University of Science and Technology of China (2013). She continued her research work in Chengdu Green Energy and Green Manufacturing Technology R & D Centre in China as a research assistant for one year. She is currently a PhD student at the Institut National de la Recherche Scientifique (INRS, Canada) with Materials and Technologies for Energy Conversion, Saving and Storage (MATECSS) excellence scholarship. Her research mainly focuses on the synthesis of semiconducting nanomaterials (such as colloidal quantum dots and nanoplatelets) and their applications in luminescent solar concentrators and solar-driven water splitting.
[20] Daniele Benetti received his B.Sc. and M.Sc. degrees in Electronic Engineering from University of Brescia (Italy). He is currently pursuing his Ph.D. in material science under the supervision of Prof. Federico Rosei at the Institut National de la Recherche Scientifique (INRS, Canada). His recent research focuses on the investigation of electronic and ionic processes of excitonic solar cells and the development of large area Luminescent Solar Concentrators (LSCs) based on quantum dots.
Dongling Ma is currently a full professor at INRS. Her main research interest consists in the development of various nanomaterials (e.g., quantum dots, catalytic nanoparticles, plasmonic nanostructures, and different types of nanohybrids) for applications in energy (e.g., solar cells), catalysis (including photocatalysis) and biomedical sectors. Before joining INRS in July 2006, she was awarded Natural Sciences and Engineering Research Council Visiting Fellowships and worked at National Research Council of Canada from 2004 to 2006. She received her Ph.D. degree from Rensselaer Polytechnic Institute (USA) in 2004.

Federico Rosei is Professor and Director of the INRS Centre Énergie, Matériaux et Télécommunications, Varennes (QC) Canada. He holds the UNESCO Chair in Materials and Technologies for Energy Conversion, Saving and Storage and the Senior Canada Research Chair in Nanostructured Materials. He received MSc and PhD degrees from the University of Rome "La Sapienza" in 1996 and 2001, respectively. He has received several awards and is Fellow/Member of many prestigious societies and academies, including the Royal Society of Canada, the European Academy of Sciences, the American Physical Society, the World Academy of Arts and Science, the Chinese Chemical Society (Honorary), the American Association for the Advancement of Science, SPIE, the Canadian Academy of Engineering, ASM International and the Engineering Institute of Canada.