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Efficient and stable tandem luminescent solar concentrators based on carbon dots and perovskite quantum dots

Haiguang Zhao[a,b,*], Daniele Benetti[b], Xin Tong[b,c], Hui Zhang[b], Yufeng Zhou[b], Guiju Liu[a], Dongling Ma[b], Shuhui Sun[b], Zhiming M. Wang[c], Yiqian Wang[a,*], Federico Rosei[b,c,**]

[a] College of Physics & The State Key Laboratory, Qingdao University, No. 308 Ningxia Road, Qingdao 266071, PR China
[b] Centre Énergie Matériaux Télécommunications, Institut National de la Recherche Scientifique, 1650 Boulevard Lionel-Boulet, Varennes, Québec, Canada J3X 1S2
[c] Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, PR China

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ABSTRACT

Luminescent solar concentrator (LSC) can serve as large-area sunlight collectors, suitable for applications in building-integrated high-efficiency and low-cost photovoltaics. Inorganic perovskite quantum dots (QDs) are promising candidates as absorbers/emitters in LSCs, due to their high quantum yields (close to 100%), possibility of tuning size and chemical composition and broad absorption spectrum and high absorption coefficient. However, despite their great potential for technological development, LSCs fabricated using colloidal perovskite QDs still face major challenges such as low optical efficiency and limited long-term stability. Here we report a large-area (~ 100 cm^2) tandem LSC based on nearly reabsorption-free carbon dots (C-dots) and inorganic mixed-halide perovskite QDs spectrally-tuned for optimal solar-spectrum splitting. The as-fabricated semi-transparent device, without involving any complicated processes, exhibits an external optical efficiency of ~ 3% under sunlight illumination (100 mW/cm^2), which represents a 27% enhancement in efficiency over single layer LSCs based on $CsPb(Br_xI_{1-x})_3$ QDs and 117% over $CsPb(Cl_xBr_{1-x})_3$ QDs. Our work shows that the addition of C-dots can dramatically enhance the long-term durability of LSC devices based on perovskite QDs due to their excellent photostability and simultaneous absorption of ultraviolet light.

1. Introduction

Solar technologies, including photovoltaic (PV) devices and systems for hydrogen production, represent a promising opportunity to address the increasing demand for clean and renewable energy [1–4]. However, there are still several challenges that hinder the widespread deployment of these technologies, specifically: (a) low efficiencies of power conversion, (b) limited stability and (c) cost which is still too high to be competitive with other sources of energy. Overall, solar electricity generated by commercial PV devices is still considered comparatively expensive [5]. Luminescent solar concentrators (LSCs) can serve as low-cost large-area sunlight collectors for PV devices which could reduce the cost of electricity by decreasing the use of expensive PV materials and modules, also enhancing the power conversion efficiency (PCE) of PV devices thanks to the enhanced photon density incident onto the PV devices, which enhances their photocurrent [6–11].

A typical LSC consists of an optical waveguide (e.g. polymer or glass) embedded with highly emissive fluorophores [6–11]. Following the absorption of sunlight, the fluorophores re-emit photons, which are then guided by total internal reflection towards PV devices positioned at their edges, where they are converted into electricity by a solar cell (Fig. 1) [6–11]. LSCs can be made flexible and are low-cost, light-weight, and semi-transparent compared with commercial silicon or other PV panels [6–11]. LSCs may be used in building-integrated PV applications, such as transparent or semi-transparent solar roofs, solar facades, and space PV applications [12,13].

Compared with organic dyes/polymers [14,15], colloidal semiconductor nanocrystals (NCs) including inorganic quantum dots (QDs) such as core/shell PbS/CdS and CdSe/CdS QDs, inorganic perovskite NCs, carbon dots (C-dots), and doped quantum wells have recently emerged as more promising and efficient emitters in LSCs [7–13,16–19]. This is due to their high photoluminescence quantum yield (PL QY), size/chemical composition-tuneable broad absorption spectrum, narrow PL spectrum, high absorption coefficient and solution processability [7–13,16–19]. In addition, the overlap of their absorption and emission spectra can be engineered and minimized so as to

* Corresponding authors at: College of Physics & The State Key Laboratory, Qingdao University, No. 308 Ningxia Road, Qingdao 266071, PR China
** Corresponding author at: Centre Énergie Matériaux Télécommunications, Institut National de la Recherche Scientifique, 1650 Boulevard Lionel-Boulet, Varennes, Québec, Canada J3X 1S2
E-mail addresses: hgzhao@qdu.edu.cn (H. Zhao), yqwang@qdu.edu.cn (Y. Wang), rosei@emt.inrs.ca (F. Rosei).

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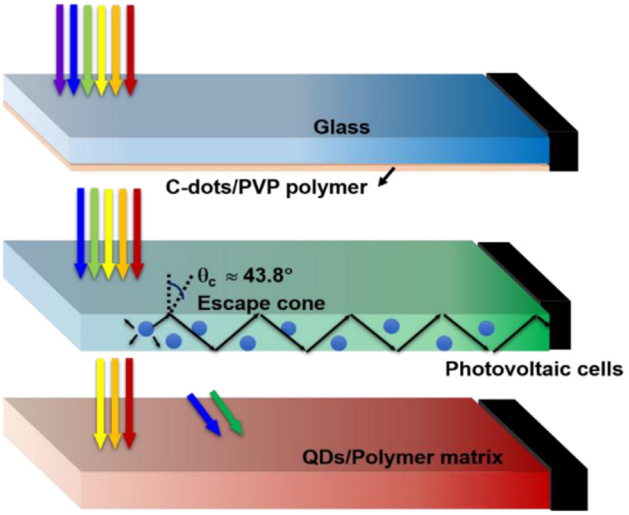

Fig. 1. C-dot and perovskite QDs based tandem LSCs. Scheme of a typical thin film LSC configuration with C-dots/polymer spin coated on a glass substrate (top). Scheme of mixed-halide perovskite $CsPb(Br_{1-x}Cl_x)_3$ QDs (middle) and $CsPb(Br_xI_{1-x})_3$ QDs (bottom) based LSCs by incorporating QDs into a polymer matrix.

suppress the energy loss caused by reabsorption [7–13,16–18]. Colloidal organic-inorganic and inorganic perovskite NCs have been synthesized [9,20–24] and were used as emitters for LSCs applications [9,23,24] in view of their high brightness with a PL QY up to 100% [25]. LSCs based on mixed-halide inorganic perovskite $CsPb(I_xBr_{1-x})_3$ QDs exhibit an external optical efficiency (defined as the ratio between the optical power of re-emitted photons reaching the edges of an LSC and the optical power of incident photons, also named PCE) of 2% with a lateral size of 1.3 × 7 cm^2 [9]. However, despite their great potential for technological development, LSCs fabricated using colloidal perovskite QDs still face the following major challenges: 1) the obtained external optical efficiency is still low compared with LSCs based on inorganic QDs (such as CuInSeS/ZnS and Si) [12,26]; ii) long-term stability of LSCs based on perovskite QDs is still limited by the stability of the perovskite materials themselves, due to their high sensitivity to moisture and ultraviolet (UV) light [20–24].

Current research efforts focus on improving the performance of LSCs by solving key challenges related to several types of energy loss: 1) a fraction of the absorbed light is re-emitted due to the non-unity PL QY of emitters; 2) reabsorption caused by the overlap between the absorption and emission spectra of the fluorophores; 3) the escaped emitted light as the refractive index of the polymer (or glass) is typically less than 1.5 (~ 75% of the emitted light trapped in an LSC waveguide), with the remainder ~ 25% lost from the top or bottom escape cone defined by Snell's Law (Fig. 1) [8,12,13]. Thus, the key requisite in terms of optical properties of fluorophores in high efficiency large-area LSCs includes high PL QY, minimal absorption and emission spectral overlap and broad absorption with significant overlap with the solar spectrum. Besides the energy loss in LSCs, the long-term stability of LSCs is still an open issue. The emitters used for LSCs easily degrade when exposed to environmental conditions, such as high humidity, UV light and high temperature (up to 100 °C) *etc* [7,13].

Several types of QDs were used as emitters to enhance the external optical efficiency of LSCs by improving their PL QY and engineering their Stokes shift (defined as the difference between the band maxima of absorption and emission spectra) [7,10,11,13,26]. For example, colloidal inorganic QDs including CdSe/CdS [13], CdSe/CdPbS [11], CdSe/CdZnS [7], CuInSeS/ZnS [12], PbS/CdS [10] and Si [26] exhibit a large Stokes shift in the 200–800 meV range and high PL QY in the range of 40–70%, leading to a conversion efficiency per incident photon of 1% in LSCs based on CdSe/CdS QDs (LSC dimensions: 21.5 × 1.3 × 0.5 cm^3) [13], 1.15% in LSCs based on CdSe/CdPbS QDs (LSC dimensions: 9 × 1.3 × 0.2 cm^3) [11] and 2.8% in LSCs based on Si QDs [26] (LSC dimensions: 12 × 12 × 0.26 cm^3). The currently reported record efficiency [3.2% in QDs [12] based LSC (12 × 12 × 0.2 cm^3) and 7.1% in dye [27] based LSC (5 × 5 × 0.5 cm^3)] is still well below the theoretical efficiency limit (21%) of LSCs as well as the target efficiency threshold for commercial products (10%) (Table 1) [28].

Table 1
Optical performance of reported LSCs based on QDs, C-dots and dyes.

Type of luminophore	Luminophore	LSC size (cm^3)	External optical efficiency	Ref.
QDs	CdSe/CdS	21.5 × 1.35 × 0.5	0.60%	[13]
QDs	$CuInSe_xS_{2-x}$/ZnS	12 × 12 × 0.3	3.20%	[12]
QDs	Silicon	12 × 12 × 0.26	2.85%	[26]
QDs	$CdSe/Cd_{1-x}Zn_xS$	90 × 30 × 0.16	–	[7]
QDs	$CdSe/Cd_xPb_{1-x}S$	7 × 1.5 × 0.3	1.40%	[11]
QDs	PbS/CdS	10 × 1.5 × 0.2	1.00%	[10]
QDs	Carbon Dots	2.5 × 1.6 × 0.1	4.75%	[19]
QDs (tandem)	$Mn:Cd_xZn_{1-x}S$/ ZnS + $CuInSe_2$/ ZnS	15.2 × 15.2 × 0.16	3.1%	[31]
Perovskite thin film	$CH_3NH_3PbI_3$	1.5 × 1.5 × 0.01	13.00%	[23]
Perovskite QDs	$CsPb(I_xBr_{1-x})_3$	9 × 1.3 × 0.2	2.00%	[9]
Dye (tandem)	BA241 + BA856	2 × 2 × 0.3	6.70%	[35]
Dye (tandem)	DCJTB + Pt (TPBP)	2.5 × 2.5 × 0.2	6.80%	[15]
Dye (tandem)	Lumogen F Red305 Fluorescence Yellow CRS040	5 × 5 × 0.5	7.10%	[27]
C-dots and perovskite QDs (tandem)	Carbon dots $CsPb(I_xBr_{1-x})_3$ $CsPb(Cl_xBr_{1-x})_3$	10 × 10 × 0.2	3.05%	This work

In addition to enhancing the PL QY and increasing the Stokes shift of QDs, a tandem structured LSC was demonstrated theoretically [29] and experimentally [15,27], improving the light absorption efficiency and decreasing the energy loss due to the light emitted because of the escape cone (Fig. 1). As already shown in the case of multiple-junction solar cells [30], or tandem LSCs based on dyes [15], absorbing different portions of the solar spectrum using different layers of emitters allows to realize high efficiency multi-layered LSCs compared with standard single-layer LSCs. For instance, dye based tandem thin film LSCs exhibit a PCE of 7.1% (with a diffusive back reflector) [27], which represents the highest reported for LSCs so far. However, the overall areas of tandem LSCs based on dyes are quite small, typically less than 25 cm^2, which is not suitable for the practical implementation of this technology [15,27]. To the best of our knowledge, there are until now only two reports for tandem LSCs using colloidal QDs [17,31]. Although inorganic perovskite QDs [9] and C-dots [19] have been separately used as emitters for single-layer LSC, there is still no report for fabricating tandem LSC by using a combination of perovskite QDs with C-dots. The rationale of combining them is that the C-dots will improve photostability of the perovskite-LSC because C-dots have a very good photostability under UV light.

Here we demonstrate the simultaneous use of C-dots with large Stokes shift and mixed-halide inorganic perovskite QDs as highly emissive fluorophores in high performance large-area (~ 100 cm^2) tandem LSCs. Specifically, we initially synthesized C-dots absorbing sunlight in the UV region via a hydrothermal approach (details included in the experimental section). The C-dots dispersed in methanol or water were subsequently mixed with polyvinylpyrrolidone (PVP) and spin-coated on a glass substrate. Then we synthesized mixed-halide $CsPb(Br_{1-x}Cl_x)_3$ and $CsPb(Br_xI_{1-x})_3$ perovskite QDs via a hot-injection approach and incorporated them into poly (lauryl methacrylate-*co*-ethylene glycol dimethacrylate) (PLMA-*co*-EGDA) polymer matrix, resulting in a semi-transparent composite. The as-fabricated semi-transparent tandem LSC based on C-dots and mixed-halide perovskite