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Stable Tandem Luminescent Solar Concentrators based on CdSe/CdS Quantum Dots and Carbon Dots

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1. Experimental Section

Chemicals and materials: S (100%), oleylamine (OLA), oleic acid (OA), and octadecene (ODE), selenium pellet (≥99.999%), Rhodamine 6G, lauryl methacrylate, ethylene glycol dimethacrylate, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, polyvinyl pyrrolidone (PVP, MW: 50000), citric acid, urea, NaOH, hexane, toluene, methanol, and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd.. Cadmium oxide (99%), Trioctyl phosphine oxide (TOPO) and trioctyl phosphine (TOP) (97%) were purchased from Sigma-Aldrich. All chemicals were used as purchased.

Synthesis of CdSe QDs: Cd-oleate (0.38 mmol, 1 mL) and TOPO (1 g) in 8 mL of ODE were purged by nitrogen at 110 °C for 30 min. Then the temperature was raised to 300 °C. The mixture of TOP-Se (4 mmol, 4 mL), 3 mL of OLA and 1 mL of ODE at room temperature was quickly injected into the Cd-oleate suspension under vigorous stirring. Subsequently, the reaction temperature dropped to 270 °C. After 5-min reaction, the reaction cell was quenched with ice water. Ethanol was added, and then the suspension was centrifuged and the supernatant was removed. The QDs were dispersed in toluene or hexane for further characterization or shell coating.

Synthesis of CdSe/CdS QDs: In a 100 mL round-bottom flask, OLA (5 mL), ODE (5 mL) and CdSe QDs (~ 2×10^{-7} mol in hexane) were degassed at 110 °C for 30 min. The reaction flask was re-stored with N_2 and the temperature was further raised to 240 °C under stirring. The $Cd(OA)_2$ dispersed in ODE (0.25 mL, 0.2 M) was added dropwise and the mixture was allowed to react for 1 h, followed by dropwise addition of 0.2 M sulfur in ODE with same volume. The shell was further annealed for 10 min. All subsequent shells were annealed at 240 °C for ~10 min following the injection of sulfur and for ~60 min following the injection of the $Cd(OA)_2$. The addition volumes of sulfur/$Cd(OA)_2$ for shell addition cycles 1-13 were as follows: 0.25, 0.36, 0.49, 0.63, 0.8, 0.98, 1.18, 1.41, 1.66, 1.92, 2.2, 2.51 and 2.8 mL, respectively. The reaction flask was cooled down to room temperature using ice water. Ethanol was added, and then the suspension was centrifuged and the supernatant was removed. The QDs were then dispersed in toluene for further characterization.

Synthesis of C-dots: 1 g citric acid and 2 g urea were dissolved in 10 mL dimethylformamide under stirring. Subsequently, the precursors were transferred into an autoclave and reacted for 6 h at 160 °C. After cooling to room temperature, the mixture was then added dropwise to 50 mL toluene to precipitate the C-dots. The precipitates were collected and dispersed in 60 mL methanol. The solution in 15 mL plastic tube was centrifuged at 6000 rpm for 3 min and the supernatant was collected for further use. For the Na^+ treatment, the purified product was mixed with 20 mL NaOH aqueous solution (50 mg/mL), stirred for 1 min. The mixture was then added dropwise to 50 mL toluene to precipitate the C-dots. The precipitates were dispersed in 60 mL methanol. The purified solution was transferred into dialysis bags with a molecular weight of 3000 Da for 2 h. The C-dots/methanol solution inside the dialysis bag was collected by opening the dialysis bag and pouring the solution into a plastic tube.

LSCs based on C-dots/PVP thin film on a glass substrate: The C-dots dispersed in methanol were mixed with PVP methanol solution with a final PVP concentration of 200 mg/mL. The concentration of C-dots is around 15 mg/mL. The mixture was then spin-coated on a glass substrate at a speed of 500 r.p.m. and an acceleration rate of 800 r.p.m./s for one min with a thickness of 50-100 μm. The glass thickness is around 2 mm.

LSCs based on CdSe/CdS QDs/PLMA polymer: The LSCs were fabricated by embedding the QDs in the polymer matrix. Typically, CdSe/CdS QDs (50 mg) dispersed in toluene were added to a 50 mL flask and the solvent was pumped away. The monomer precursors of lauryl methacrylate and ethylene glycol dimethacrylate were mixed at a mass loading of ~20%. Then the mixture solution was mixed with a UV initiator (diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide) and sonicated until a clear solution (3 mL) was obtained. The solution was then transferred into the flask containing solvent free CdSe/CdS QDs. The mixture was homogeneously dispersed by ultrasound treatment, and then injected into a model consisting of two glass slides separated by a flexible silicon rubber spacer with a thickness of ~1.8 mm. The mixture was kept under UV illumination for different hours.

External optical efficiency characterization: The external optical efficiency of the LSCs was measured by using a solar simulator at AM 1.5G (100 mW/cm^2) calibrated using a reference Si solar cell. During the measurement, the light intensity was measured using a power meter (Newport Model 843-R) which was directly coupled on one side of edges without using any optical devices, such as lens or fibers (Figure

S1). In the other setup, a Si solar cell (IXYS KXOB22) was positioned at one side of LSC edges. The current-voltage (I-V) characteristics of the fabricated LSC was measured by a Keysight 2900A Source Meter under simulated sunlight using a solar simulator at AM1.5G (100 mW·cm^{-2}).

The external optical efficiency (η_{opt}) of LSCs can be estimated using the following equation[1,2],

$$\eta_{opt} = \frac{P_{out}}{P_{in}}$$

where P_{out} and P_{in} are the power coming out of the edge of the LSC and coming in through the top surface.

When characterizing an LSC with PV cells attached, η_{opt} can be simply defined as:

$$\eta_{opt} = \frac{I_{LSC}}{I_{SC} \times G}$$

where I_{LSC} and I_{SC} are the short circuit current from the Si diode coupled with the LSC and from the Si diode under direct illumination, and G is the geometric factor.

Table S1 The power output (P) obtained from the power meter and the calculated external optical efficiencies (η) for single-layer and tandem LSCs based on C-dots and CdSe/CdS QDs under one sun illumination (100 mW/cm^2).

LSCs	**QDs**	**P (mW/cm^2)**	**η(%)**
Single (10×10×0.2 cm^3)	C-dots	8.75	0.7±0.1
Single (10×10×0.18 cm^3)	CdSe/CdS QDs	16.6	1.2±0.1
Tandem (10×10×0.38 cm^3)	C-dots	8.75	0.7±0.1
	CdSe/CdS QDs	9.7	0.7±0.1

2. Figures

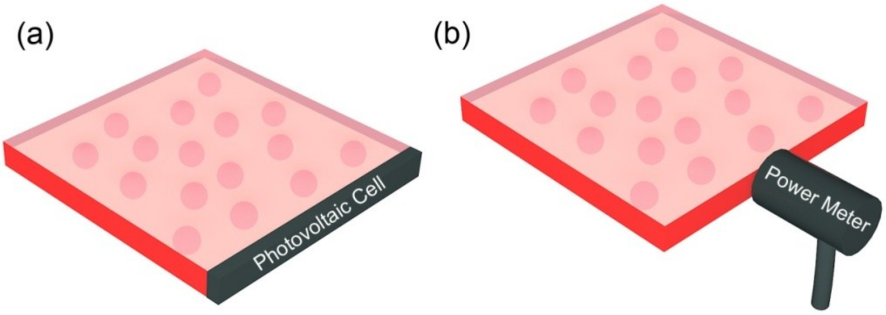

Figure S1 Scheme of the two different configurations used for characterizing the efficiency of the LSC. (a) A Si cell is coupled with one edge of the LSC. (b) A power meter directly coupled on one edge of the LSC to measure the light intensity.

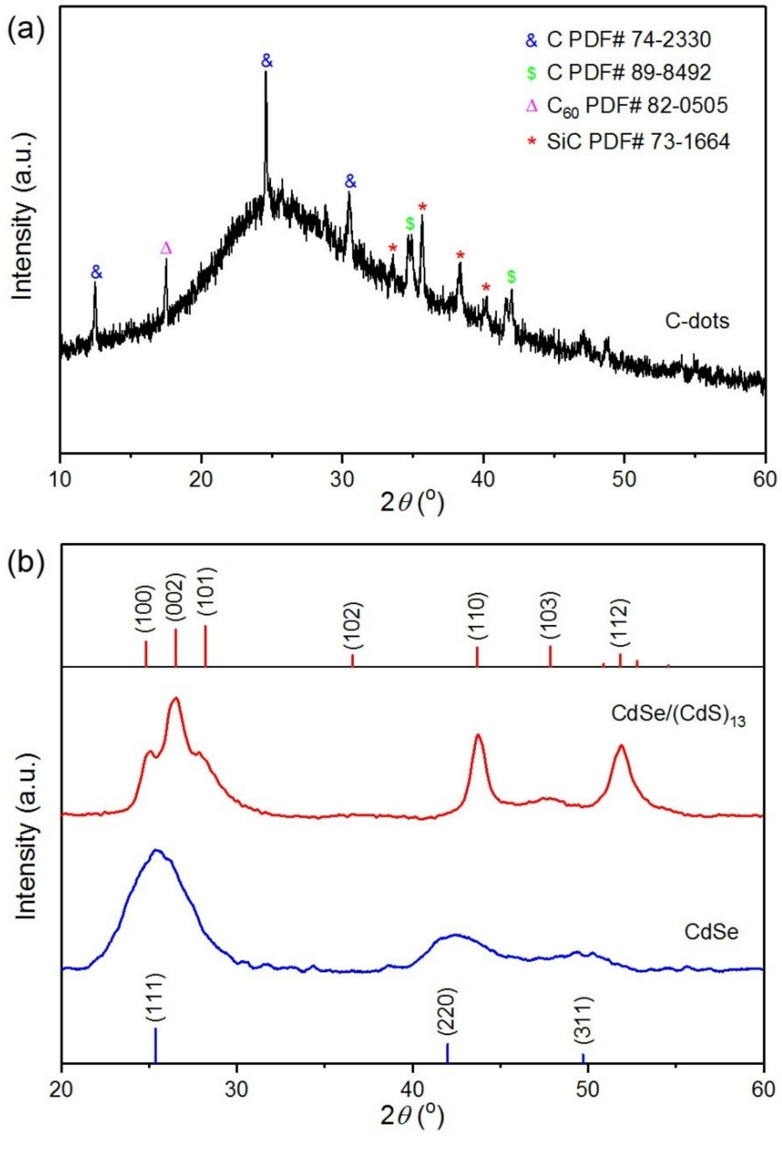

Figure S2 XRD patterns for C-dots (a), CdSe QDs and CdSe/CdS QDs (b).

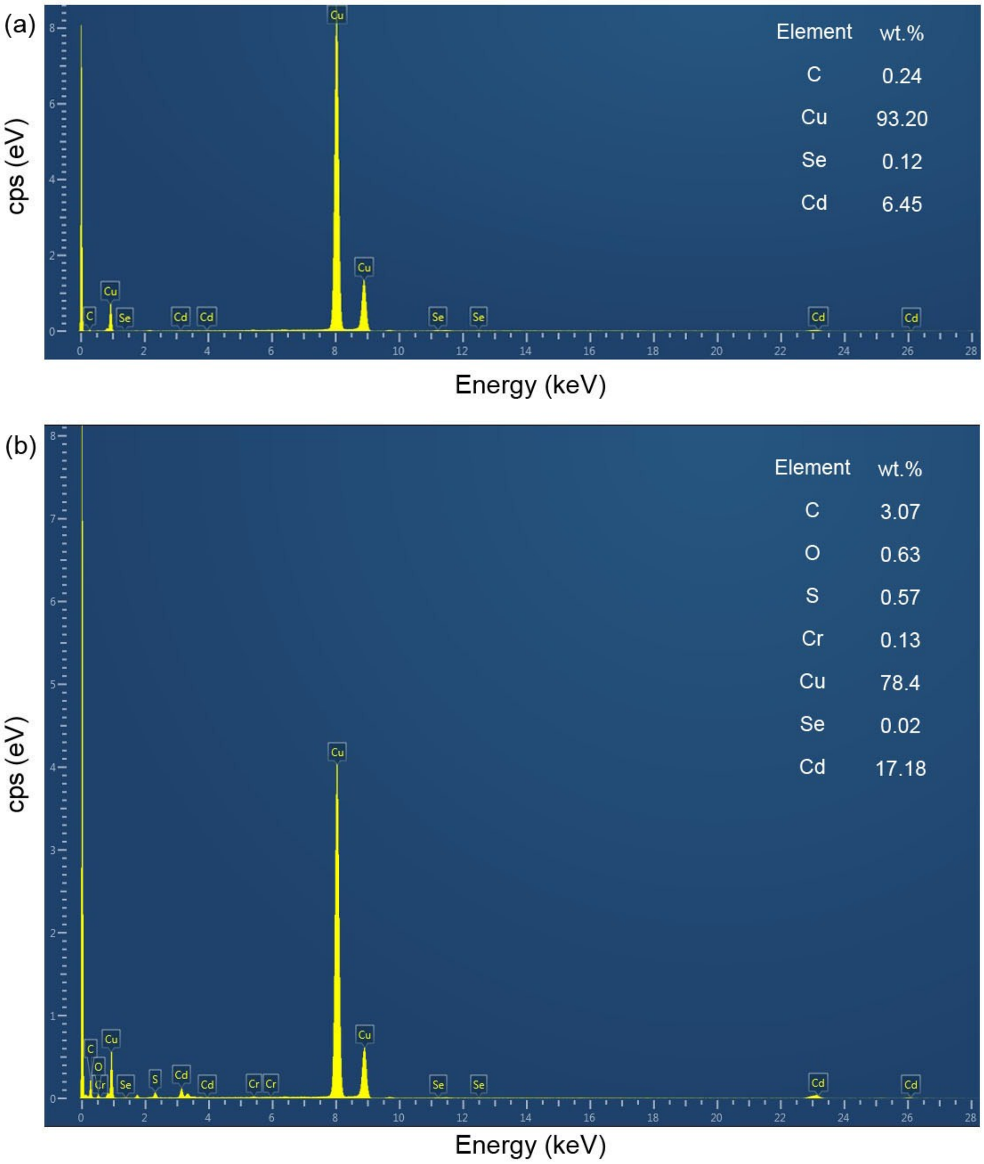

Figure S3 EDS spectra of chemical compositions with relative mass concentration for CdSe QDs (a) and CdSe/CdS QDs (b).

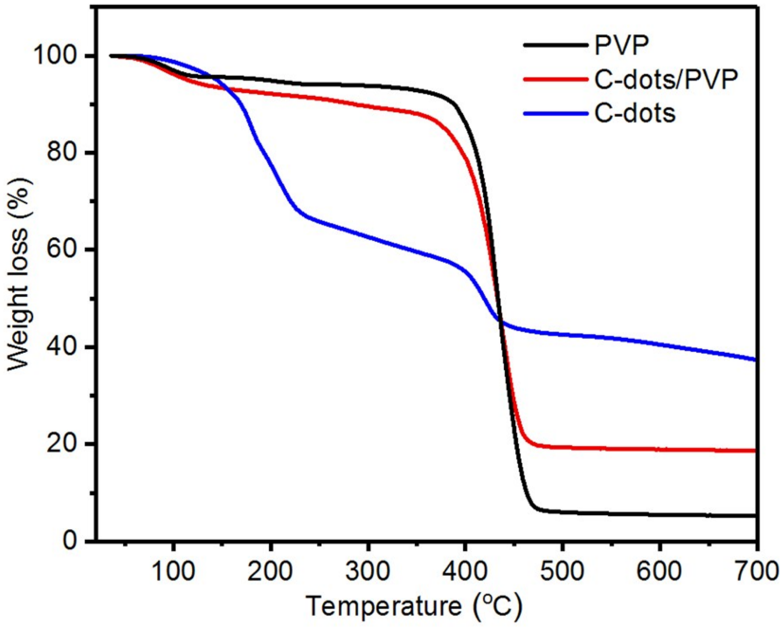

Figure S4 TGA curves of C-dots, PVP and C-dots/PVP hybrid.

The thermogravimetric analysis (TGA) was carried out in a flow of nitrogen at 10 ^{o}C/min. Weight loss at different temperatures indicates the decomposition as well as thermal stability of the samples. For the three samples, weight loss before 120 ^{o}C is likely due to the removal of absorbed water or crystalline water. In case of pure PVP, consistently, weight loss between 370 ^{o}C and 470 ^{o}C is due to the pyrolysis and carbonization of PVP. The total weight loss of PVP reaches 95% from room temperature to 700 ^{o}C. The pure C-dots show multiple losses in weight. Initial weight loss is ascribed to water molecules associated with C-dots. Subsequently, two step weight losses were observed. The weight loss of approximately 35% was observed between 120 ^{o}C and 300 ^{o}C, which can be speculated due to the loss of functional groups (carboxyl group or amide group) associated with C-dots surface. Further weight loss of 20% (300 ^{o}C~450 ^{o}C) may be due to the burning of carbon. The total weight loss of C-dots reaches 63% from room temperature to 700 ^{o}C. Unlike the C-dots, the C-dots/PVP conjugate shows a steady weight loss between 370^{o}C and 470 ^{o}C, which is similar to that of PVP due to the low concentration of C-dots.

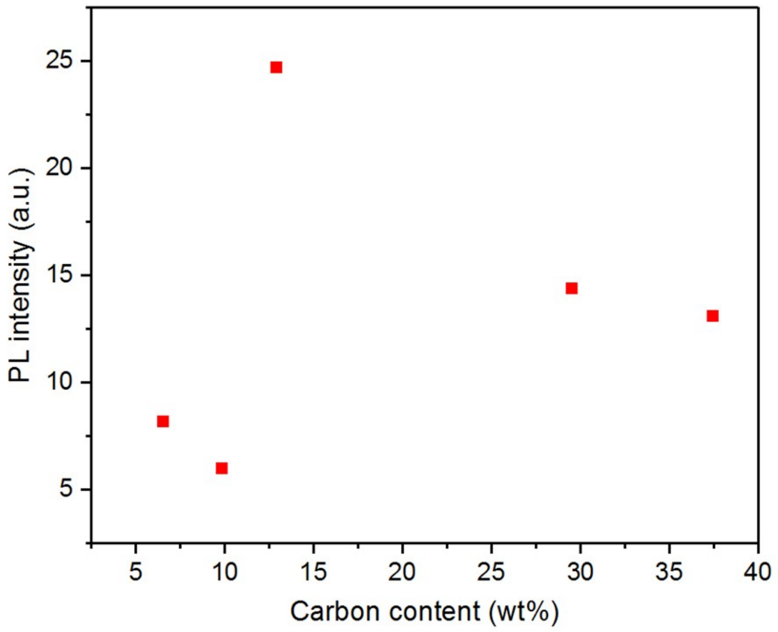

Figure S5 Plot of PL intensity of high-energy emission peak as a function of the C-dots concentration in PVP.

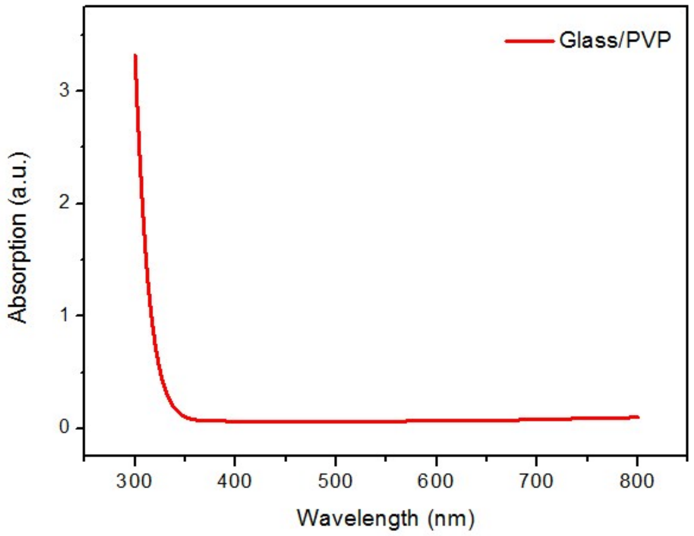

Figure S6 Absorption of PVP polymer on a glass substrate.

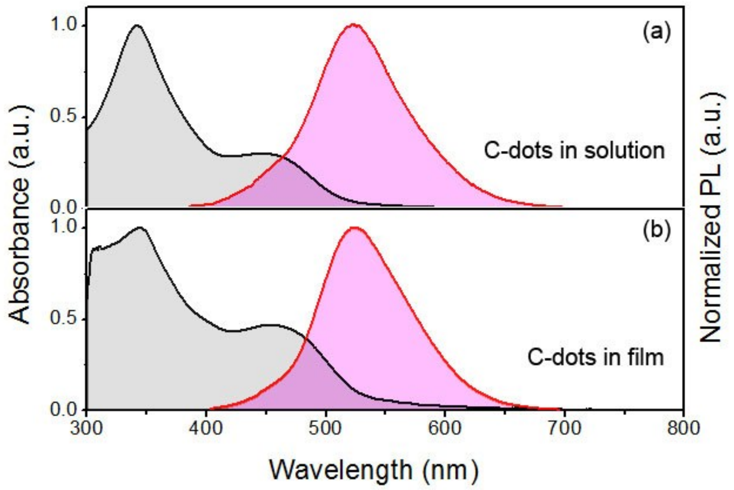

Figure S7 Normalized absorption and emission spectra for C-dots in solution (a) and film (b).

References

1 F. Purcell-Milton and Y. K. Gun'ko, *J. Mater. Chem.*, 2012, **22**, 16687-16697.

2 H. Zhao, D. Benetti, L. Jin, Y. F. Zhou, F. Rosei and A. Vomiero, *Small*, 2016, **12**, 5354-5365.