

Exciton recycling via InP quantum dot funnels for luminescent solar concentrators

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Synthesis of indium phosphide QDs: Indium chloride (InCl_3) (99.999%), hexadecylamine (HDA) (98%), zinc undecylenate (98%), stearic acid (SA) ($\geq 98.5\%$), 1-Octadecene (ODE) (90%), tris(trimethylsilyl)phosphine ($\text{P}(\text{TMS})_3$) (95%), copper(II) acetate ($\text{Cu}(\text{Ac})_2$) (98%) and zinc dithiolcarbamate (97%) were purchased from Sigma-Aldrich. ODE was purified at 120 °C by evacuation and refilling with nitrogen for 1 h. A stock solution of $\text{P}(\text{TMS})_3$ in ODE was prepared with the concentration of 0.2 mmol.mL⁻¹ and stored in inert atmosphere at -20 °C. For the synthesis of green emitting InP cores, firstly, 0.1 mmol indium chloride (InCl_3), hexadecylamine (HDA), stearic acid (SA) and 3 ml 1-octadecene (ODE) were mixed in a nitrogen (N_2)-purged glovebox. The solution was heated up to 120°C and repeatedly evacuated and refilled with nitrogen to obtain oxygen and moisture-free environment. Then, the flask was heated up to 220 °C and 0.5 ml tris(trimethylsilyl)phosphine solution ($\text{P}(\text{TMS})_3$) (0.2 mmol.mL⁻¹ in ODE) was injected to the flask. The temperature was decreased to 200 °C and kept for 20 min. Afterwards, the flask was cooled down to room temperature. For ZnS shelling, 0.15 mmol zinc dithiolcarbamate and 2 ml ODE were added to the InP core solution and heated up to 200°C for 20 min to facilitate ZnS shell growth. Finally, the flask was cooled down to 50°C and 4 ml toluene was added and centrifuged in 4,000 rpm for 5 min. The clear supernatant solution was discarded. The QDs were separated by adding ethanol/acetone followed by centrifuging in 8,000 rpm for 15 min. The final product was dispersed in toluene and stored in inert atmosphere. For yellow and red emitting QDs, the phosphine injection temperature was 260°C and 280°C, respectively. For copper doping, the temperature was reduced down to 180 °C after InP core formation and then 1 μmol copper stearate was introduced to the solution and then heated up to 220 °C and kept for 20 min.

Fabrication of nanoassemblies: Precleaned glass substrates (6 cm × 6 cm × 2 mm) were activated by UV-ozone treatment. QD layers and 3-mercaptopropionic acid (3-MPA) (0.1 wt % in methanol) as the linker were spin-coated at 4000 rpm. The fabrication technique was also used by the following references [S1–S3].

Steady-state optical characterization and time-resolved fluorescence spectroscopy: The absorbance, photoluminescence and PLQY measurements of the colloidal QDs and fabricated LSCs were carried out by Edinburgh Instruments FS5 spectrofluorometer. For the absorbance, photoluminescence and PLQY of the colloidal QDs, standard quartz cuvettes with the cross dimensions of 1 cm × 1 cm were used. For the PL measurement, samples were excited by Xe lamp at the excitation wavelength of 375 nm. (The excitation and emission bandwidths were set as 2 nm and 3 nm, respectively.) The integrating sphere was used to measure absolute PLQY of the synthesized colloidal QDs and fabricated nano assemblies. (The excitation and emission bandwidths were set as 7 nm and 0.26 nm, respectively.) For the fluorescence stability test, nanoassemblies were kept under dark condition between the two consecutive PLQY measurements. Time-resolved measurements were carried out by Picoquant MicroTime 100 confocal fluorescence microscope. The excitation beam was provided by 8 mW picosecond diode laser heads operating at 375 nm.

Femtosecond pump-probe spectroscopy: The non-linear absorption properties and ultrafast decay dynamics of the InP core QD and copper-doped InP QD were investigated by using a femtosecond pump-probe spectrometer (Helios, Ultrafast Systems). The QD solution was excited at 320 nm by using the fourth-harmonic output of a tunable, femtosecond optical parametric amplifier (OPA, TOPAS Prime, Spectra-Physics), which was pumped with a 2-mJ, 800-nm Ti^{3+} : sapphire regenerative amplifier (pulse duration: 120 fs, pulse repetition rate: 1 kHz, Spitfire Ace, Spectra-Physics). A portion of the 800 nm output of the regenerative amplifier was further focused inside a sapphire plate to generate the femtosecond white light continuum probe pulses in the 430-800 nm wavelength range. The white light continuum probe was split into two beams before passing through the sample. One of them was

directly sent to the sample and the other beam was used as a reference to monitor the fluctuations in the generated white light continuum intensity during the measurements. In the pump-probe spectroscopy experiments, the pump and probe beams were overlapped and focused inside a 10 mm long quartz cuvette, containing the QD solution with the optical density of 1 at the band-edge absorption. The average number of electron-hole pairs (N_{e-h}) generated during the pumping process was calculated from $N_{e-h} = J/J_{sat}$, where J is the photon fluence and the saturation fluence J_{sat} is given by $h\nu_{pump}/\sigma_a$ [S4]. During the pump-probe experiments, the 320 nm fluence (J) incident on the QDs was sufficiently low ($240 \mu J/cm^2$), giving $N_{e-h} = 0.5$. Bi-exponential fitting was applied to the decaying part of the measured nonlinear absorbance to extract the fast and slow decay times of the undoped and copper-doped QDs. Figure S1 shows the time-resolved variation of the nonlinear absorbance of the undoped InP QDs at the probe wavelength of 570 nm. Figure S2 further shows the contour plots of the nonlinear absorbance ΔA as a function of the probe wavelength and probe delay for the (a) undoped core and (b) copper doped InP QDs. Copper doping leads to faster decay rates as discussed in the main text.

Performance analysis of the LSCs: For the external quantum efficiency measurements, a calibrated Newport Oriel LCS-100 solar simulator AM 1.5 G was used according to the reference [S5]. Silicon solar cell with dimensions of $11 \times 7 \text{ cm}^2$ was used for the efficiency measurements of QD-LSCs. Since the surface area of solar cell was greater than LSC edge area, a black tape was used to mask the excessive area. During the measurement, the uncoupled edges of the LSCs were covered with black paint and only one edge was coupled to the solar cell in order to eliminate any incident light from outside and PL reflection back to the waveguide. LSCs were illuminated with the power density of 100 mW.cm^{-2} and the short-circuit current from the illumination of the solar cell (J_{PV}) and with the LSC (J_{LSC}) was measured. The optical gain factor was measured based on $G = L / (4D)$, in which L is the side length of LSC (6 cm) and D is the thickness of the QD-LSC equal to 2 mm. As a result, the G factor of the fabricated LSC was determined to be 7.5. To gain more insight into the performance enhancement, we compared the optical quantum efficiency (η_{OQE}), (Equation S1-S3). The trapping efficiency (η_{trap}) is the efficiency of light trapping inside the waveguide modes. In the case of spatially isotropic light emitters such as the InP-based QDs in this study, the trapping efficiency can be calculated based on Equation 9 [S6], where θ_c is the total internal reflection angle of the LSC architecture and is dependent on the refractive index based on Equation S4, where n is the refractive index of the substrate (*i.e.*, commercial glass), which was considered as 1.51. As a result, the total internal reflection angle and trapping efficiency corresponded to 41.5° and 74.9%, respectively.

$$EQE = \eta_{OQE} \times \eta_{abs} \text{ (Equation S1)}$$

$$\eta_{OQE} = \eta_{PL} \times \eta_{trap} \times \eta_{wg} \text{ (Equation S2)}$$

$$\eta_{TIR} = \cos(\theta_c) \text{ (Equation S3)}$$

$$\theta_c = \arcsin\left(\frac{1}{n}\right) \text{ (Equation S4)}$$

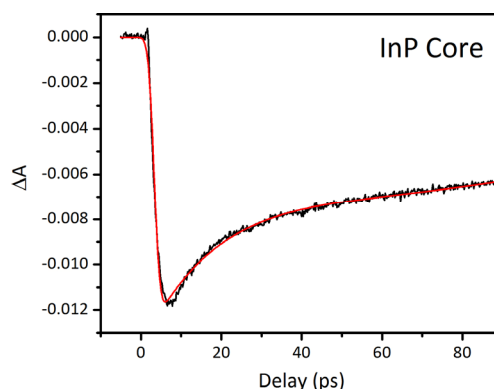


Figure S1 Time-resolved variation of the nonlinear absorbance of the undoped InP QDs at the probe wavelength of 570 nm.

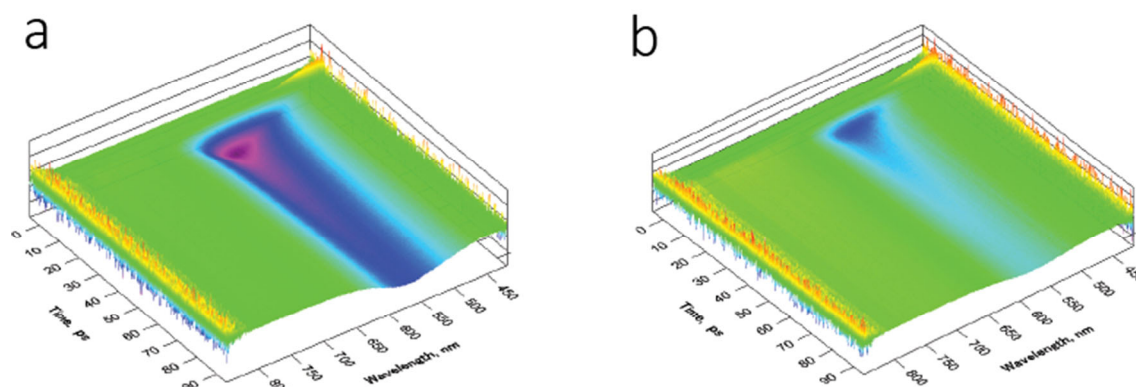


Figure S2 Contour plots of the nonlinear absorbance ΔA as a function of the probe wavelength and probe delay for the (a) undoped core and (b) copper doped InP QDs.

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