

Origin of Unusual Excitonic Absorption and Emission from Colloidal Ag₂S Nanocrystals: Ultrafast Photophysics and Solar Cell

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Supporting Information

Chemicals:

Silver Nitrate (AgNO₃, 99.8%), Cadmium oxide (CdO, 99.995%), 3-Mercaptopropionic acid (3-MPA, ≥99%), Oleic acid (OA, 90%, technical grade), 1-Octadecene (ODE, 90%), Sulfur (99.998%), Trioctylphosphine (TOP, 97%), Cadmium nitrate tetrahydrate (98%), sodium sulfide hydrate (>99%), and potassium chloride (>99%) were purchased from Sigma Aldrich. Toluene (99.5%), Dimethyl sulphoxide (DMSO, 99.9%), Methanol (99.5%), Acetonitrile (99.8%), Propan-2-ol (98%) were purchased from Rankem India Ltd, Ethanol (99.9% AR, S D Fine chem. Ltd.). Titanium tetrachloride was obtained from Merck. F-doped SnO₂ (FTO) coated glass (~ 7 ohm/sq) was obtained from Aldrich. Transparent titania paste (DSL-18NR-T, diameter ~20 nm), scattering titania paste (WER2-O, diameter 150-250 nm) were obtained from Dyesol.

Synthesis of CdS Nanocrystals (NCs):

CdS NCs with average diameter 1.6 to 4.1 nm were prepared following ref¹. 0.4 mmol CdO, 1 ml Oleic acid (OA) and 16 ml octadecene (ODE) was degassed (under alternate vacuum and N₂ atmosphere) at 120 °C for about half an hour with slow stirring. The reaction temperature was then set to 300 °C under N₂ atmosphere. A separate solution of 0.2 mmol S in 2 ml ODE was

quickly injected to the above solution at 300 °C under N₂ atmosphere. The reaction was stopped at different times to yield different sizes of CdS NC. These NCs were then precipitated and washed two times using propan-2-ol and finally redispersed in toluene.

Reversible cation exchange of CdS NCs \rightleftharpoons Ag₂S NCs. CdS NCs were subjected to undergo cation exchange by treating dilute dispersion of CdS NCs in toluene with concentrated methanolic solution of AgNO₃ (keeping Cd²⁺: Ag⁺ ratio of 1:4), following ref². Drop by drop addition of methanolic solution of AgNO₃ to CdS NC dispersion changes the color of dispersion from light yellow to dark brown/black indicating formation of Ag₂S at room temperature. Whereas, reverse cation exchange from Ag₂S to CdS was done at elevated temperature around 80-90 °C. A dilute dispersion of Ag₂S NCs in toluene and 0.2 ml trioctylphosphine (TOP) was heated to 80 °C under inert atmosphere, followed by injection of excess Cd((NO)₃)₂ in acetonitrile. A slower color change from dark brown to light yellow takes place indicating the formation of CdS nanocrystals. Tributylphosphine (TBP) is known as a better reagent compared to TOP for this purpose, and is expected to give better reproducibility.

Characterization. Steady-state PL and PL decay dynamics using time correlated single photon counting (TCSPC) technique were recorded using Edinburgh FLS980 instrument using liquid nitrogen cooled NIR PMT detector. PL quantum yield (QY) was measured using Indocyanine green as a reference dye (QY in DMSO 12%)³. UV-visible-NIR absorption spectra of NCs were recorded using a Perkin Elmer, Lambda-45 UV/Vis/NIR spectrometer. Bruker D8 Advance X-ray diffractometer equipped with copper K_α (1.54 Å) radiation was employed to obtain powder XRD data. TEM images were collected using a JEOL JEM 2100F microscope operated at 200 kV. Fourier-transform infrared (FTIR) spectra were obtained by employing NICOLET 6700 FTIR spectrometer (Thermo scientific).

Z-scan data analysis: To quantitatively determine the TPA coefficient (β) we have theoretically modeled our Z-scan data. The differential equation describing the nonlinear absorption can be written as

$$\frac{dI}{dz} = -\beta I^2 \quad (1)$$

where z and I are position and intensity respectively. Solving equation 1 for a pulsed Gaussian beam, the nonlinear transmission in the Z-scan experiment can be written as

$$T = e^{-\alpha_0 L} (1-R)^2 / p_0 \sqrt{\pi} * \int_{-\infty}^{+\infty} \ln \left(\sqrt{1 + p_0^2 e^{-t^2}} + p_0^2 e^{-t^2} \right) dt \quad (2)$$

where, L and R are the sample length and surface reflectivity respectively, and p_0 is given by

$$p_0 = \sqrt{2 \left(\gamma (1-R) I_0^2 L_{eff} \right) / \left(1 + (Z/Z_0)^2 \right)} . \quad I_0, Z_0, L_{eff} = (1 - e^{-\alpha_0 L}) / \alpha_0 \quad \text{and } \alpha_0 \text{ are the on-axis peak intensity, intensity, Rayleigh length, effective length intensity independent (linear) absorption coefficient respectively.}$$

Preparation of TiO₂ coated FTO electrode Ag₂S Quantum Dot Sensitized Solar Cell (QDSSC): FTO coated glass (Aldrich, $\sim 7 \Omega/\text{sq}$) was cleaned sequentially with soap solution (30 min), water (30 min) and ethanol (30 min) using an ultrasonication bath. Finally cleaned FTO coated glass was heated at 450 °C for 10 minutes in order to remove organic contaminants. The compact layer of TiO₂ was prepared on top of conducting surface of FTO glass. For that 0.04 M aqueous solution of TiCl₄ was poured on conducting surface so that the glass would fully dip into the solution and then the glass was heated at 80 °C for 30 min in dipped state. Then the FTO glass was cleaned by water and finally with ethanol. The mesoporous TiO₂ active film was then prepared by doctor blading method using commercial TiO₂ paste (Dyesol DSL-18NR-T, diameter ~ 20 nm). Over the active TiO₂ layer, a scattering layer of TiO₂ (Dyesol WER2-O, diameter 150-250 nm) was doctor bladed. The film was sintered at 450 °C for 30 minutes for each layer. The heating and cooling process for the TiO₂ electrode preparation was gradual to prevent the crack formation on film. After all, the sintered TiO₂ film was treated with aqueous TiCl₄ (0.04 M) and finally sintered again at 450 °C for 30 min in order to remove pin holes and cracks from the TiO₂ film. The thicknesses of active and light scattering layers were optimized to $\sim 10 \mu\text{m}$ and $\sim 4 \mu\text{m}$ respectively.

Supporting Figures:

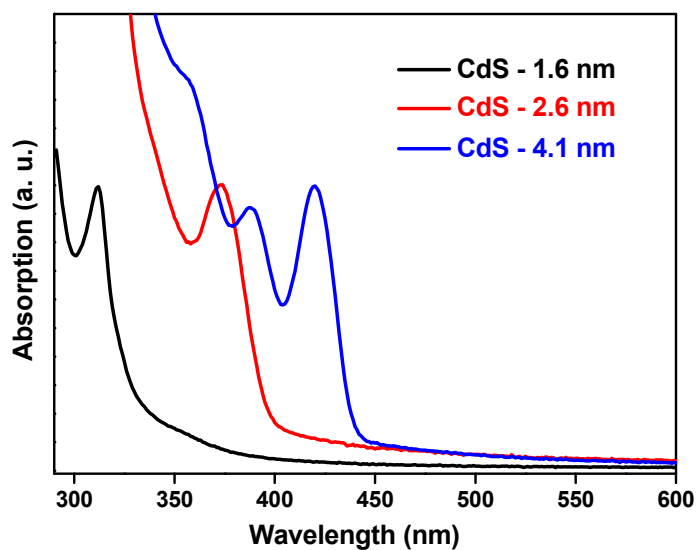


Figure S1: Steady state electronic absorption spectra of CdS nanocrystals with different sizes. Average diameter of CdS NCs were estimated to be 1.6 nm (black line), 2.6 nm (red line) and 4.1 nm (blue line) from the absorption spectra using ref⁴.

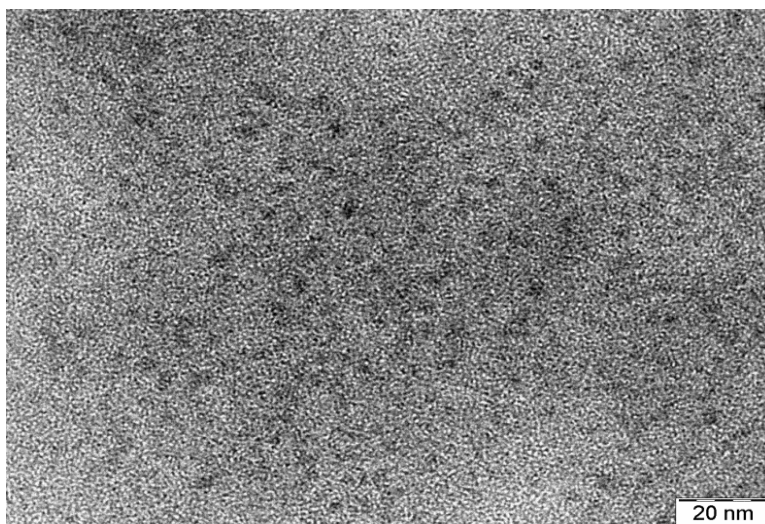


Figure S2: TEM image of CdS nanocrystals with lowest excitonic absorption at 375 nm (red spectrum in Figure S1)

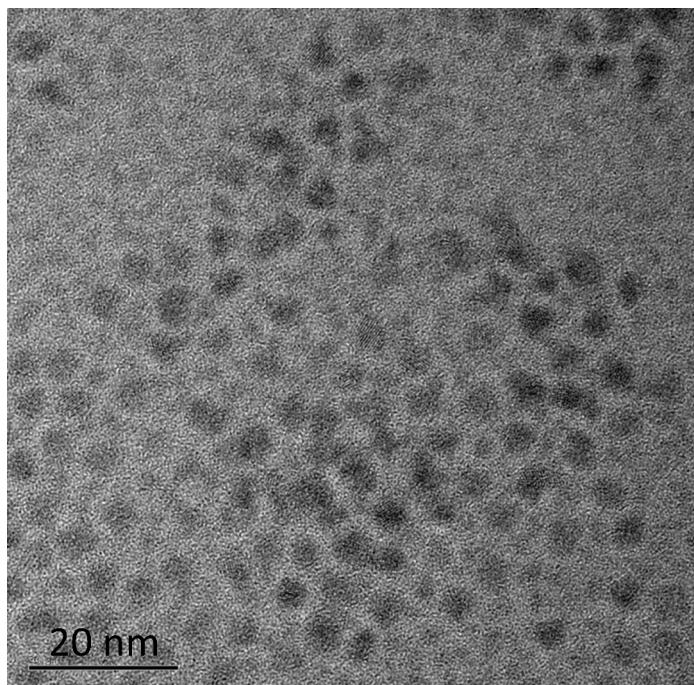


Figure S3: TEM image of CdS nanocrystals with lowest excitonic absorption at 421 nm (blue spectrum in Figure S1)

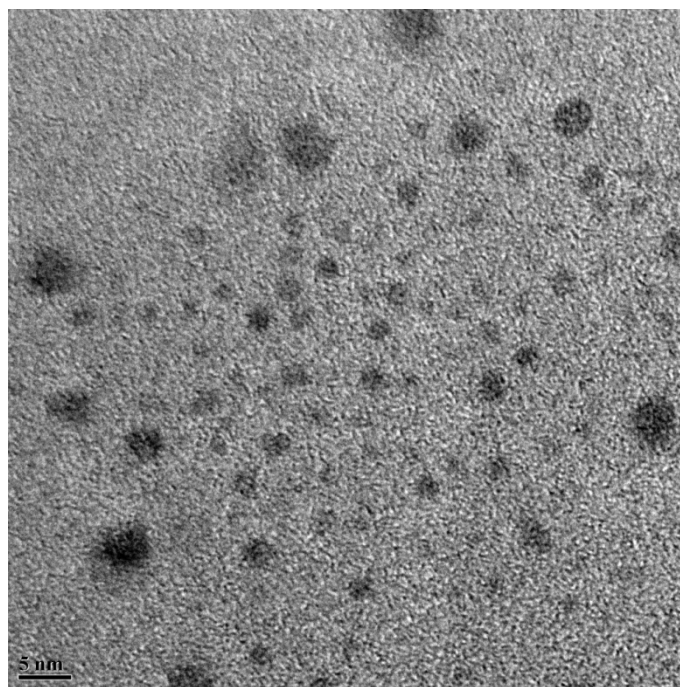


Figure S4: TEM images of Ag₂S nanocrystals obtained by employing cation exchange of CdS nanocrystals of average size 4.1 nm.

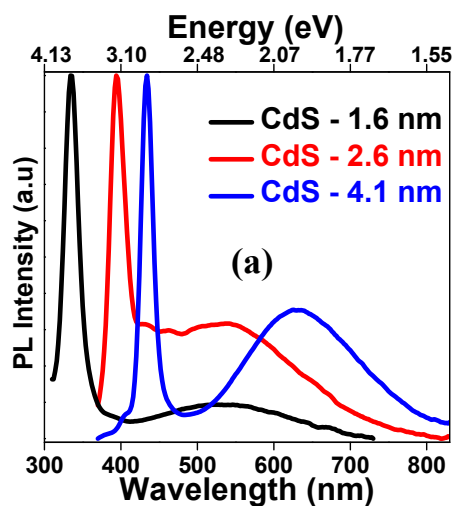


Figure S5: Photoluminescence (PL) spectra of three different sizes of CdS NCs.

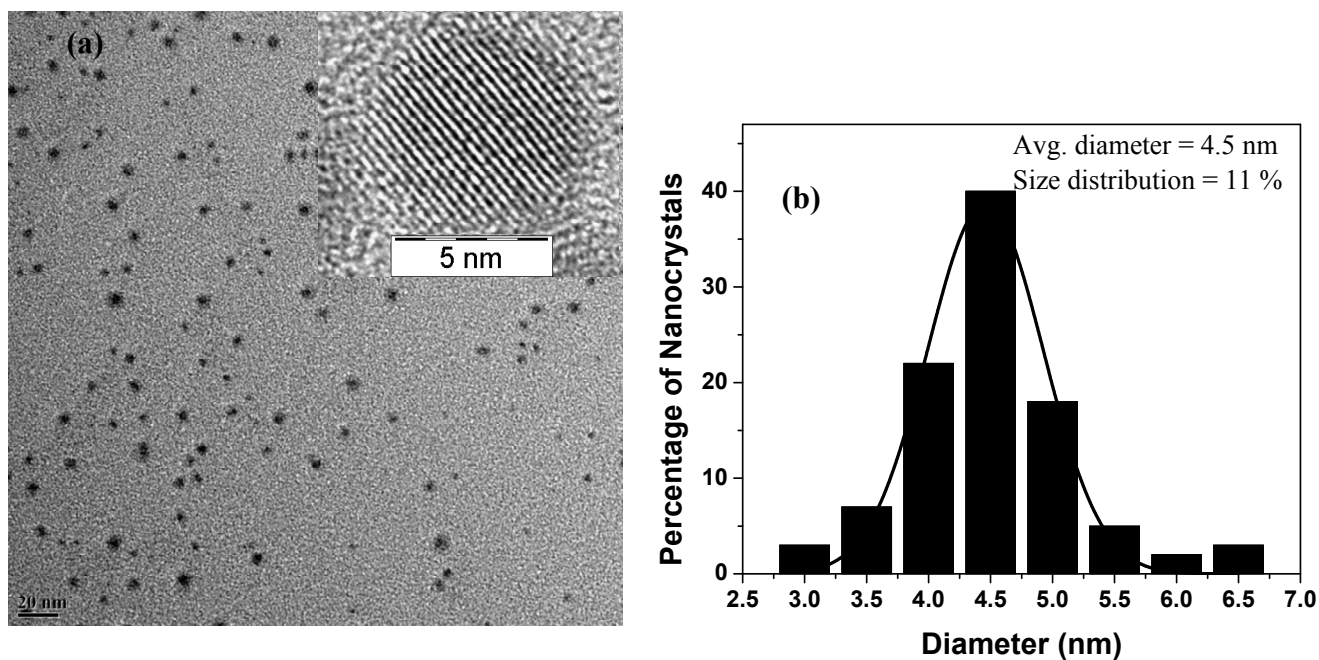


Figure S6: (a) TEM image, inset shows high resolution TEM image and (b) size distribution plot of Ag₂S NCs for reaction done at 145 °C using molecular precursors as starting material.

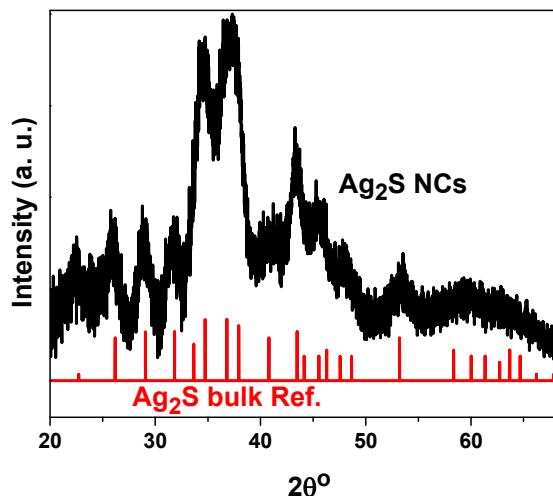


Figure S7: XRD pattern of Ag_2S NCs synthesized from molecular precursors at 145°C , with 10 minute reaction time.

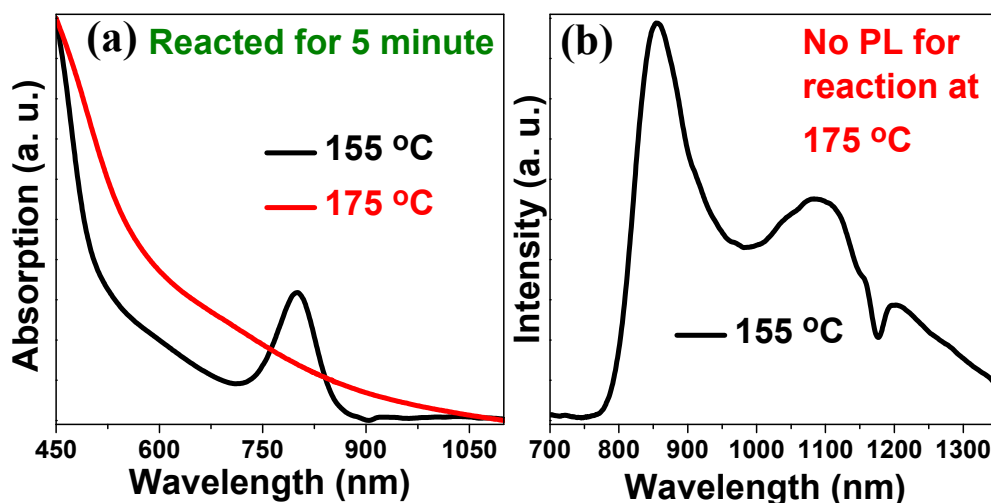


Figure S8: (a) Electronic absorption and (b) PL spectra of Ag_2S nanocrystals obtained after 5 min of reaction at 155°C and 175°C . At reaction temperature of 155°C , sharp excitonic absorption is observed after 5 min, however, PL spectrum shows defect-related emission (1090 nm) along with excitonic emission (855 nm). When the reaction temperature was increased to 175°C , a feature-less bulk-like absorption is observed along with no detectable emission after 5 min of reaction.

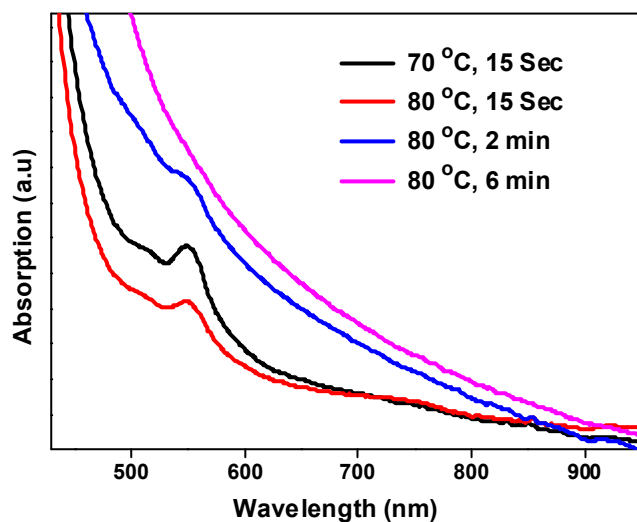


Figure S9: UV-visible-NIR electronic absorption spectra of Ag₂S NCs dispersed in DMSO. Aliquots were taken at different intervals for reactions carried out at 70 °C and 80 °C.

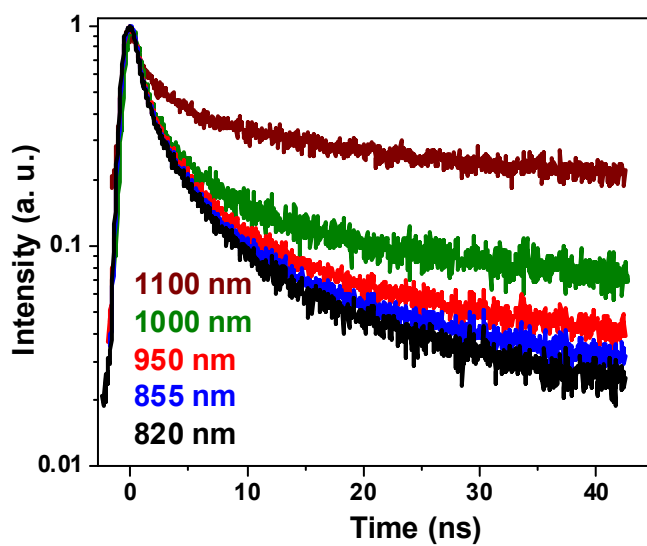


Figure S10: PL decay dynamics at different emission wavelengths as mentioned in the figure, for colloidal Ag₂S NCs prepared at 145 °C using molecular precursors.

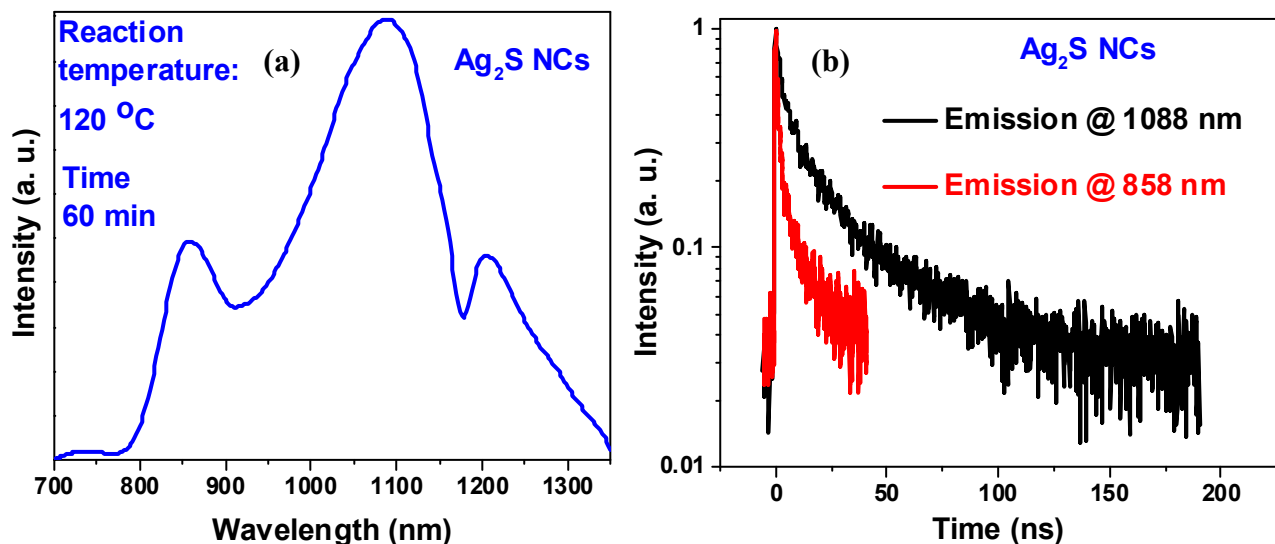


Figure S11: (a) Photoluminescence spectra from Ag_2S nanocrystals for reaction done at 120 °C with 60 min reaction time. This spectrum is also given in Figure 2b of main paper. (b) PL decay dynamics for the two emissions peaks (at 858 nm and 1088 nm), after exciting at 468 nm.

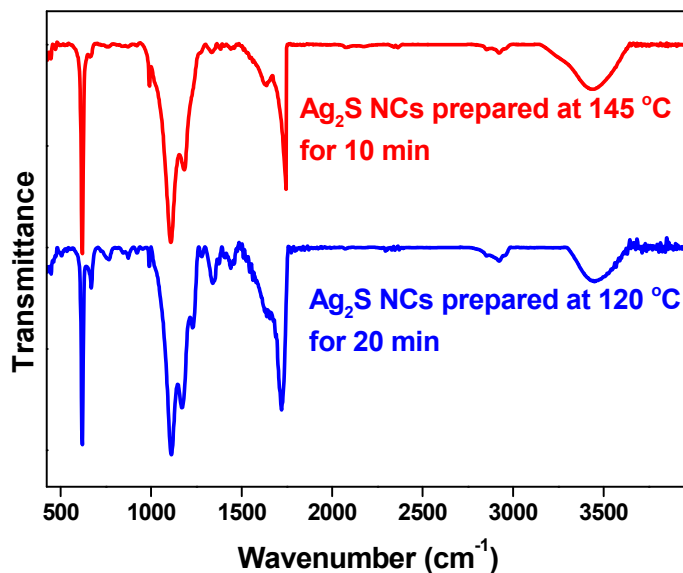


Figure S12: Comparison of Fourier-transform infrared (FTIR) spectra of 3-MPA capped Ag_2S NCs prepared under different conditions. These results suggest all 3-MPA capped Ag_2S NCs have similar surface capping.

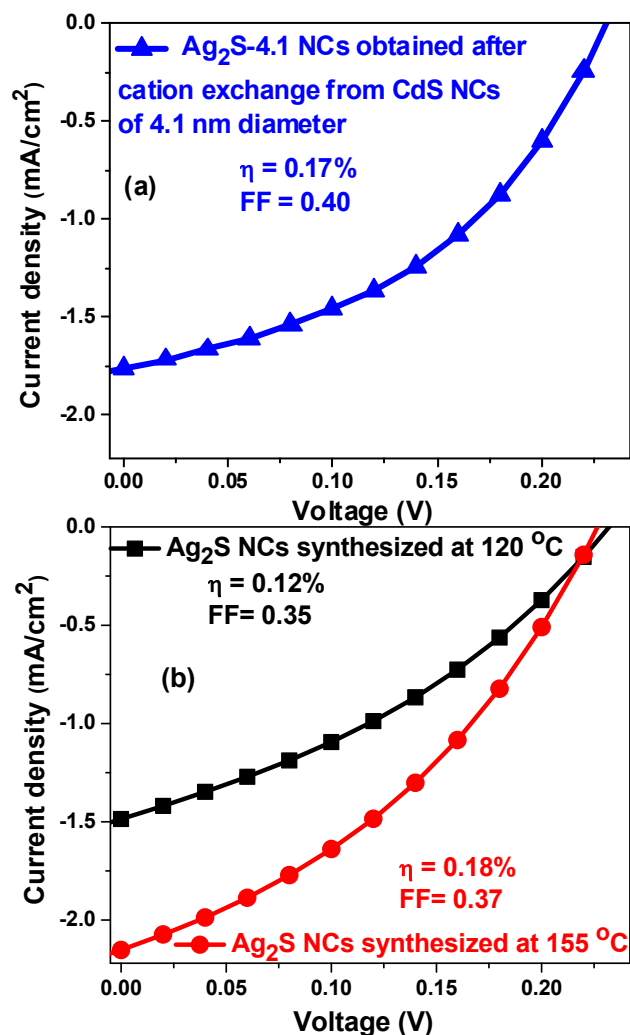


Figure S13: Current density (J) vs voltage (V) plots for QDSSCs. (a) Ag₂S NCs obtained after cation exchange of oleic acid capped CdS (4.1 nm diameter) NCs was used as sensitizer. For better charge transport, oleic acid capping ligand was exchanged with 3-Mercaptopropionic acid. (b) Ag₂S NCs obtained from direct synthesis using molecular precursors at reaction temperatures 120 °C (black curve) and 145 °C (red curve). Cell active area was kept in between 0.24 to 0.28 cm² for all cells.

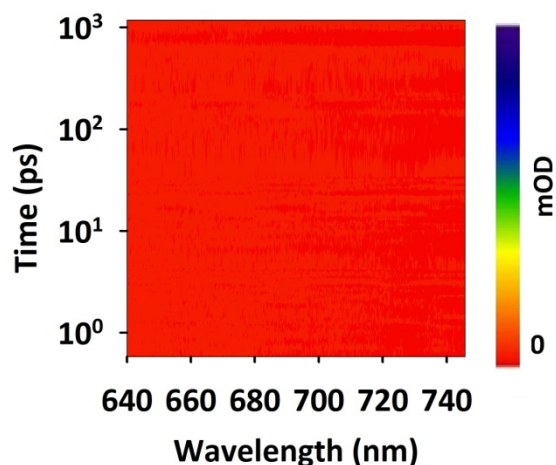


Figure S14: Contour plot of fs time resolved TA of optimized Ag₂S NCs prepared at 145 °C using 560 nm excitation.

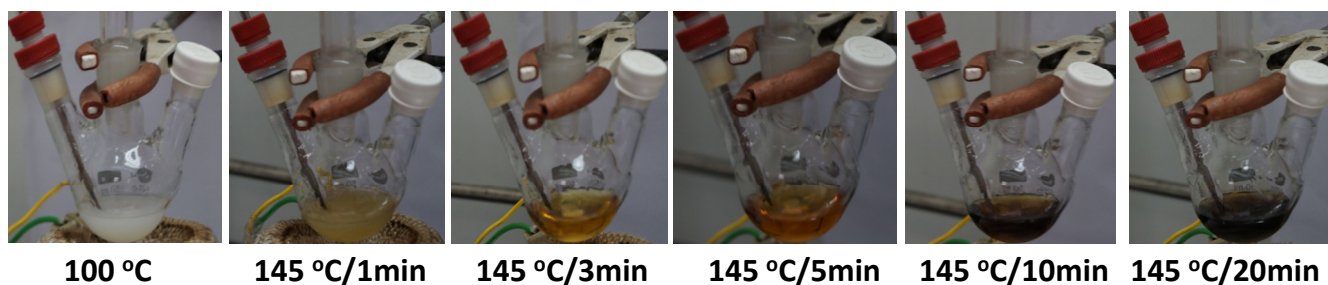


Figure S15: Photographs showing progress of reaction with change in color of the reaction mixture. The reaction mixture contains AgNO₃ dissolved in ethylene glycol, followed by injection of 3-MPA at 100 °C. Final growth temperature was set to 145 °C and photographs were taken during daylight at different intervals.

Reference:

1. Yu, W. W.; Peng, X. G. Formation of High-Quality CdS and Other II-VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers. *Angew. Chem. Int. Ed.* **2002**, *41*, 2368-2371.
2. Son, D. H.; Hughes, S. M.; Yin, Y. D.; Alivisatos, A. P. Cation Exchange Reactions-In Ionic Nanocrystals. *Science* **2004**, *306*, 1009-1012.
3. Benson, R. C.; Kues, H. A. Fluorescence Properties of Indocyanine Green as Related to Angiography. *Phys. Med. Biol.* **1978**, *23*, 159-163.
4. Yu, W. W.; Qu, L. H.; Guo, W. Z.; Peng, X. G. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003**, *15*, 2854-2860.