Luminescence and Solar Cell from Ligand-Free Colloidal AgInS$_2$ Nanocrystals †

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† Electronic Supplementary Information (ESI)

Chemicals:
Ammonium sulfide (40-48 wt% solution in water, Aldrich), formamide (FA, spectroscopy grade, Aldrich), silver nitrate (99%, Aldrich), toluene (99.5%, Rankem), ethanol (99.9% AR, S D Fine chem. Ltd), N,N-dimethyl formamide (DMF, S D Fine chem.), indium (III) nitrate hydrate (99.999%, Aldrich), acetonitrile (S D Fine chem.), terpineol (Aldrich), ethyl cellulose (Aldrich), acetic acid (Merck), sodium sulfide (Merck), sulfur powder (Merck), titanium tetrachloride (Merck), potassium chloride (Merck), F:SnO$_2$ (FTO) coated glass (8 ohm/square from Solaronix) and TiO$_2$ (P25, from Degussa). HPLC grade ethanol and methanol were used. All the Chemicals were used as received without further purification.

Synthesis of Ligand-Free AgInS$_2$ NCs:
A mixture of AgNO$_3$ (0.1 mmol, 0.0169 g) and In(NO$_3$)$_3$.H$_2$O (0.1 mmol, 0.0300 g) were dissolved in 10 mL FA in a 50 ml three neck round bottom flask. The flask was heated up to 70 °C under N$_2$ flow along with magnetic stirring for about 15 minutes. 100 µL (NH$_4$)$_2$S solution (40-48 wt% in water) was diluted by adding 1 mL FA and was injected slowly to this hot
cationic precursor solution. The reaction was carried out for 15 minutes and cooled to room temperature by removing the heat supply. The reaction mixture was then centrifuged at 5000 rpm for 5 minutes, and the supernatant liquid was collected after discarding the precipitate. Acetonitrile was added to the supernatant liquid leading to second precipitation, followed by centrifugation. The obtained second precipitate is the final AgInS$_2$ NC product discussed in this paper.

**Post-Synthesis Annealing of Colloidal AgInS$_2$ NCs:**
The supernatant liquid obtained after first precipitation as discussed above was further diluted by two times by adding fresh FA. The dilute AgInS$_2$ NC dispersion is put in to a three-neck round bottom flask maintaining inert atmosphere and subsequently heated to a desired temperature (up to 150 °C) for 15 minutes.

**Supporting Figures:**

![J-V characteristic for a cell with sample processed at 150C. Here we have used aqueous solution of polysulfide as electrolyte. This exhibit similar results but with somewhat lower J$_{SC}$ compared to methanol based polysulfide electrolyte (Figure 5c in manuscript).](figure_s1)

**Figure S1:** J-V characteristic for a cell with sample processed at 150C. Here we have used aqueous solution of polysulfide as electrolyte. This exhibit similar results but with somewhat lower J$_{SC}$ compared to methanol based polysulfide electrolyte (Figure 5c in manuscript).
Figure S2: FTIR data of AgInS$_2$ NCs synthesized at 70 °C.

Figure S3: TGA data of AgInS$_2$ NCs synthesized at 70 °C.
Figure S4: TEM images of AgInS$_2$ NCs synthesized at (a) 70 °C and (b) after annealing at 150 °C.

Figure S5: CIE diagram of AgInS$_2$ NCs processed at different temperatures. The obtained CIE coordinates are (0.48, 0.51), (0.60, 0.40) and (0.68, 0.32) for colloidal NCs annealed at 70, 125 and 150 °C respectively.
Figure S6: PL spectra of colloidal AgInS$_2$ NCs annealed at different temperatures. Spectra for NCs annealed at 70 and 150 °C were shifted horizontally by +0.19 eV and -0.145 eV in order to overlap with the spectrum for NCs processed at 125 °C.

Figure S7: (a) PL spectra of colloidal AgInS$_2$ NCs annealed at different temperatures after normalizing with corresponding absorbance at the excitation wavelength. (b) Photoluminescence decay dynamics of colloidal AgInS$_2$ NCs annealed at 70 and 150 °C after excitation at 2.7 eV (459 nm) with emission energies fixed at 2.16 and 1.82 eV respectively.
Figure S8: Electrochemical Impedance Spectroscopy (EIS) plot for a solar cell made using AgInS$_2$ nanocrystals annealed at 150 °C. The response of cells under light is shown in red dots and under dark in black squares. These devices do not exhibit any additional characteristic high frequency arc/semicircular feature related to intrinsic limitations of majority carrier transport. [Ref - A. Guerrero, S. Loser, G. Garcia-Belmonte, C. J. Bruns, J. Smith, H. Miyauchi, S. I. Stupp, J. Bisquert and T. J. Marks, Phys. Chem. Chem. Phys., 2013, 15, 16456].