Prevention of Photooxidation in Blue-Green Emitting Cu doped ZnSe Nanocrystals

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Supporting Information

Experimental and Instrumentation:

Materials:

Zinc stearate ($Zn(St)_2$, tech), Octadecylamine (ODA, 97%), Octadecene (ODE, tech.), Mercaptopropionic acid (MPA), Stearic acid (SA, 95%), Tetramethylammonium hydroxide (TMAH, 25% in methanol), S powder (99.9%), Copper(II)chloride (97%) were purchased from Aldrich. Tributylphoshphine (TBP, 97%) was purchased from Spectrochem, India. Se powder (200 mesh, 99.99%) was purchased from Alfa-Aesar. All the chemicals were used without further purification.

Synthesis of Copper Stearate:

2.84 g SA was dissolved in 20 ml of methanol in a conical flask and heated to 50 ^{o}C to get a clear solution. 2.93 g TMAH was dissolved in 5 ml methanol separately and added to the SA solution dropwise. The mixture was stirred for 20 min. 0.67 g of $CuCl_2$ was dissolved in 10 ml methanol and dropwise added to the above solution under vigorous stirring condition. Sky blue precipitate of Copper(II)stearate was flocculated which was collected by centrifugation and dried under vacuum.

Preparation of Stock Solutions:

TBPSe stock was prepared by taking 1.8 g Se powder in 8 g TBP inside a Glove-box. Sulfur stock was prepared by dissolving 0.04 g S powder in 10 ml of ODE with gently heating under Argon. $Cu(St)_2$ stock solution was prepared by dissolving 0.0634 g in 10 ml of ODE under Argon. $Zn(St)_2$ stock solution was prepared using 0.315 g $Zn(St)_2$ and 0.248 g SA in 4 ml ODE.

Cu doped Zinc Selenide/Sufide:

In a 50 ml three necked flask, 0.063 g $Zn(St)_2$ and 10 ml ODE are loaded and degassed for 15 minutes by purging with Argon at 100 ^oC. In a separate vial, 0.5 g ODA was degassed for five minutes and 0.5 ml of the TBP-Se stock solution was mixed in it. Then the reaction flask was heated to 300 ^oC and the selenium solution was injected into it at this temperature. After a desired size (preferably smaller) of ZnSe was reached, the reaction mixture was cooled to 220 ^oC to stop the growth of ZnSe. A required amount of dopant (0.1 ml $Cu(St)_2$ stock solution) was injected dropwise at that temperature and annealed for 30 min. Once the dopant emission was noticed then multilayer of ZnSe was epitaxially grown by dropwise addition of 2 ml $Zn(St)_2$ stock solution at 230 ^oC and annealed for another 30 minutes. Then another remaining $Zn(St)_2$ stock and 0.5 ml of S stock was injected dropwise at a time at 230 ^oC. Finally the temperature was increased to 250 ^oC and annealed for few minutes(10-15 minutes). After that the reaction mixture was cooled down to room temperature and nanocrystals were purified by adding acetone as non solvent and finally dispersed in chloroform for further analysis.

Water Soluble Cu and ZnSe/S by MPA Exchange:

Purified doped nanocrystals were dissolved in a minimum volume of chloroform and excess mercaptopropionic acid was added until the solutions become cloudy. The mixture was then shaken for 20 minutes. The MPA capped d-dots were flocculated, separating out the d-dots from the free MPA, which remained dissolved in chloroform. The precipitate was washed with chloroform to remove excess MPA. Finally desired amount of water was added to precipitated nanocrystals and tetramethylammonium hydroxide was dropwise added until all the nanocrystals were transferred to water.

Optical Measurements:

UV-Vis measurements were taken with a Shimadzu UV 2550 spectrophotometer. Photoluminescence spectra were collected using a Horiba Jobin Yvon Fluromax -4 spectroflurometer. The QY was measured with respect to a dye quinine sulphate using a standard procedure.

Transmission Electron Microscopy:

Tem images were taken on a JEOL-JEM 2010 electron microscopy using 200kV electron source. Specimens were prepared by dropping a drop of nanocrystal solution in chloroform on a carbon coated copper grid, and the grid were dried under in air.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES):

The dopant percentage was determined by ICP using Perkin – Elmer Optima 2100 DV machine. At first, the D-dots were repeatedly purified to remove excess precursors. Then the purified nanocrystals were dissolved in chloroform. The chloroform was then evaporated and the dried nanocrystals were digested in concentrated HNO_3. The nitric acid solution of the samples was diluted with double distilled water to do the measurements.

X-ray Diffraction (XRD):

XRD of the doped sample was taken by Bruker D8 Advance powder diffractometer, using Cu Kα (λ= 1.54 Å) as the incident radiation.

Electron Paramagnetic Resonance (EPR):

EPR measurement was done using a 9.5 GHz JEOL spectrometer operated at X-band frequency. The g value (effective Zeeman factor) is dependent on the orientation of magnetic field. The splitting of Cu doped ZnSe is anisotropic system. When the magnetic field is perpendicular to unpaired electron of Cu^{2+} system then it is called $g^{\parallel}$ and parallel to unpaired electron is $g_{\perp}$.

Lifetime Measurement:

For the time correlated single photon counting (TCSPC) measurements, the samples were excited at 370 nm using a picosecond diode laser (IBH Nanoled-07) in an IBH Fluorocube apparatus (JY-IBH-5000M). The fluorescence decays were collected on a Hamamatsu MCP photomultiplier. The fluorescence decays were analyzed using DAS6 software. The average lifetime was calculated using equation below. The data is fitted with 2nd order exponential decay.

$$y = a_1 * \exp(-x/\tau_1) + a_2 * \exp(-x/\tau_2) \quad \text{-------} \ (1)$$

X-ray Photoemission Spectroscopy (XPS) Measurement:

XPS using higher energies were performed using a commercially available X-ray photoemission spectrophotometer from VSW scientific instruments.

Supporting Figures

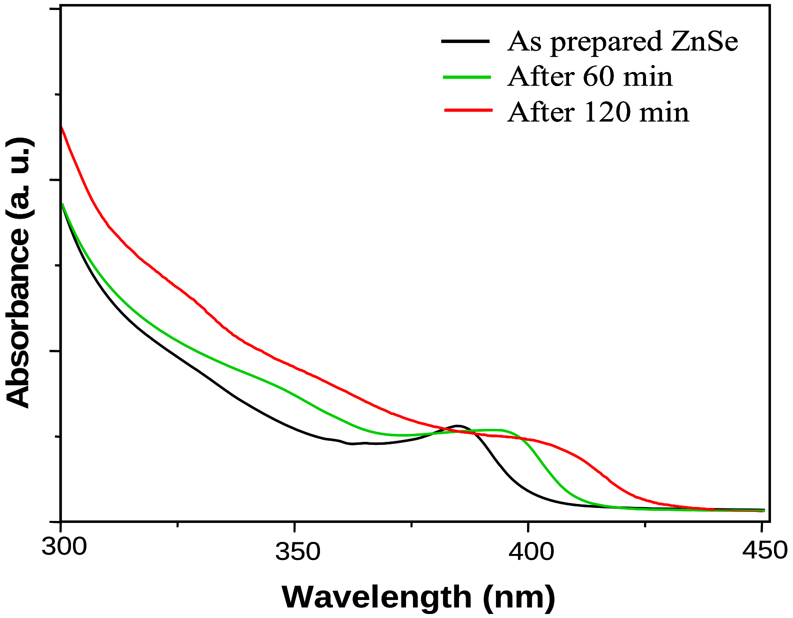

Figure S1. Absorption spectra of as prepared undoped ZnSe nanocrystals (black line). The others two absorption spectra are of Cu doped ZnSe/S system at different time interval.

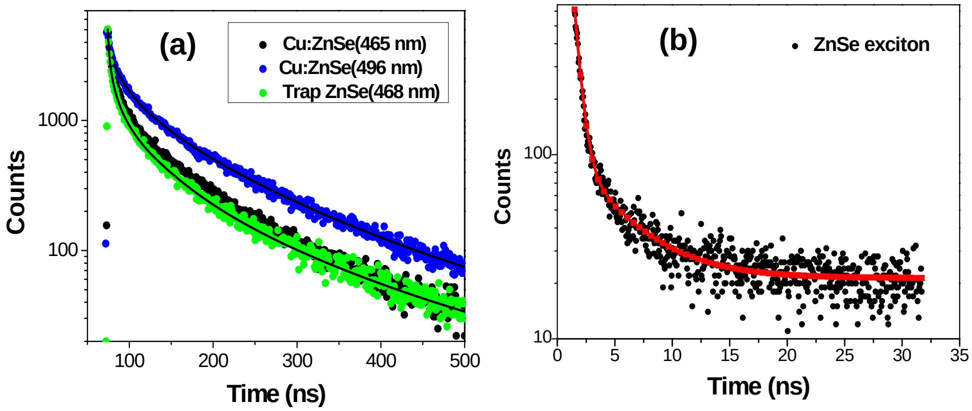

Figure S2. (a) Photoluminescence (PL) decay spectra of trap ZnSe at emission 468 nm (green dots), Cu doped ZnSe/S at emissions fixed at 465 nm (black dots), 496 nm (blue dots) which is also in fig 1b in main text respectively. All samples are synthesized at same condition. (b) PL decay spectra of ZnSe fixed at excitonic emission 410 nm. For both Y-axis is in logarithmic scale.

The life-time associated with various decay processes are listed in the Table below. It clearly shows that the exciton emission has a life-time about half a ns, while that associated with the trap emission is in the order of 10 ns. The emission collected at 460 nm from Cu doped ZnSe is most probably still dominated by the trap emissions, as indicated by the short ns range life-times. However, as the emission from Cu-doped samples are moved to longer wave-lengths, thereby reducing the overlap with the trap emissions, we find a longer than 100 ns decay channel begins to dominate the life-time plots. We associate this longer life process with emission that involves Cu d-states, as it clearly cannot be due to either excitonic or purely trap emission, both of which are much faster (≤ 10 ns) processes.

Sample	**a_1**	**τ_1 (ns)**	**a_2**	**τ_2 (ns)**
ZnSe(exciton 410 nm)	0.999	0.537	0.0106	4.79
ZnSe(trap emission at 468 nm)	0.34	1.2	0.652	7.9
Cu doped ZnSe(at 460nm)	0.301	2.7	0.699	14.2
Cu doped ZnSe(at 496nm)	0.123	25	0.55	118

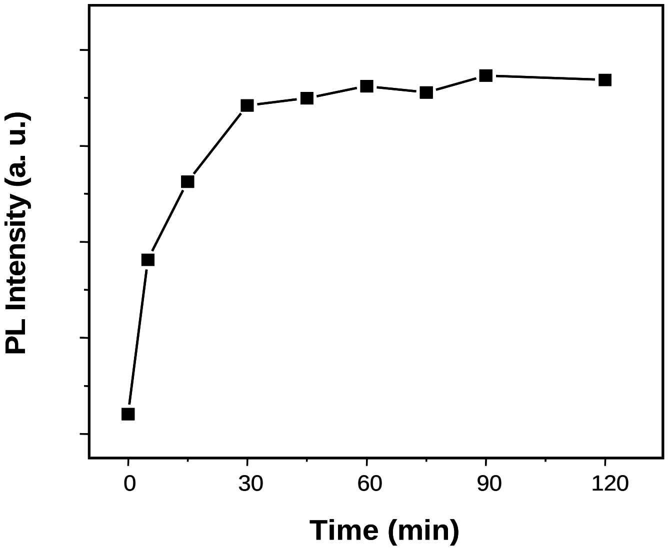

Figure S3. Temporal evolution of PL intensity of Cu doped ZnSe after tetrabutyl ammoniumborohydride addition in non aqueous medium. After adding the borohydride PL intensity increased and after certain time it was constant.

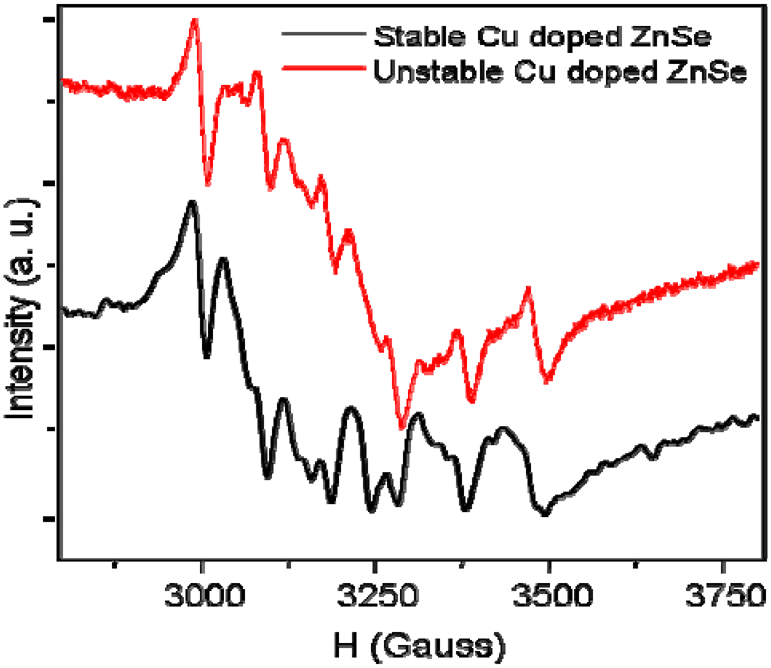

Figure S4. EPR spectrum of stable (black line) and quenched (red line) Cu doped ZnSe. From this spectrum we are confirmed that both samples have the Cu^{2+} ions. There are two types of Cu^{2+} centers and the $g\|$ value 2.1621 is greater than $g\perp$ value 1.85009, which suggested that Cu^{2+} ions are subjected to tetragonal elongation.

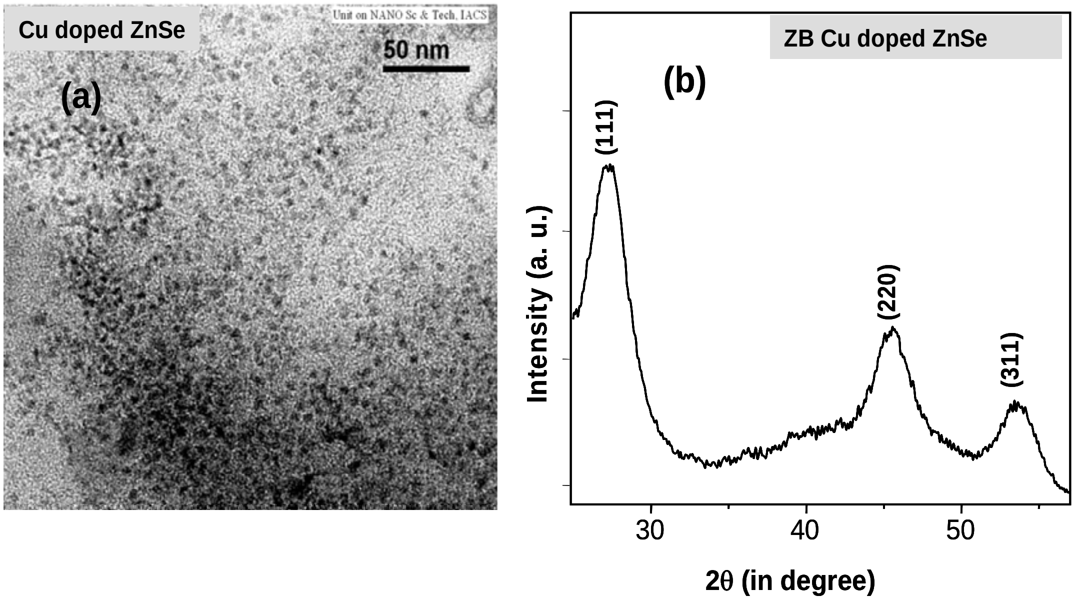

Figure S5. (a) TEM micrograph of Cu doped ZnSe nanocrystals. (b) XRD pattern of the Cu doped ZnSe, which shows the cubic structure of nanocrystals.

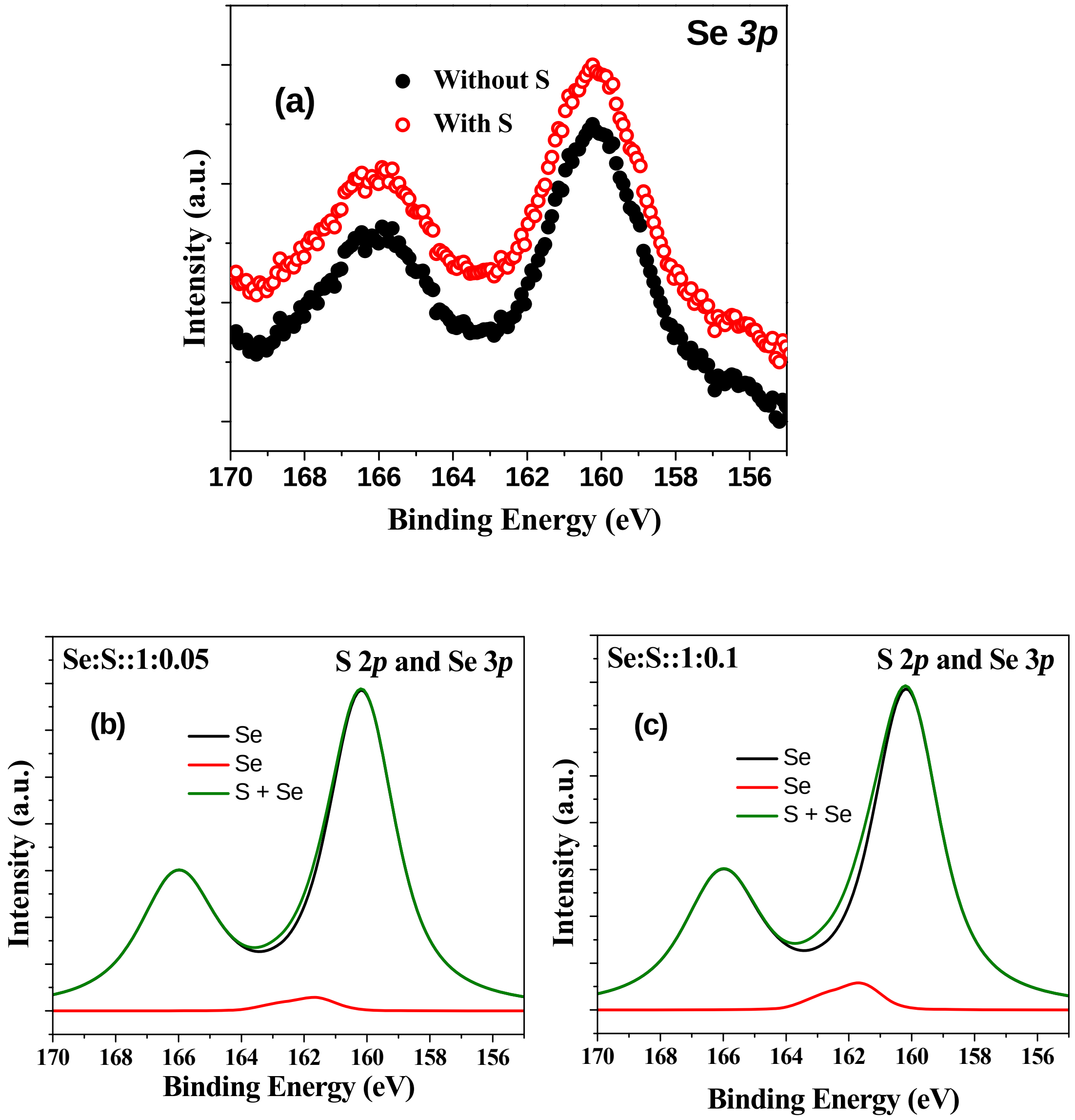

Figure S6. (a) XPS spectra Cu doped ZnSe with S and with out S. (b) and (c) Probable XPS spectrum of different S, Se ratio.