Supplementary information

Facile synthesis of composition and morphology modulated quaternary CuZnFeS colloidal nanocrystals for photovoltaic application

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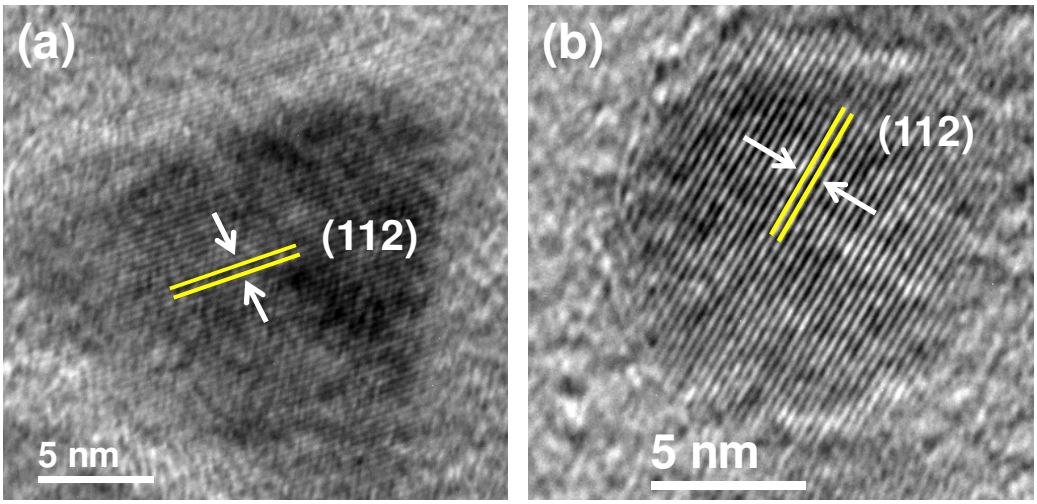


Figure S1. (a-b) High-resolution transmission electron microscope (HRTEM) images of CZIS NCs showing well resolved interplanar distance corresponds to the (112) plane of chalcopyrite crystal structure. Here CZIS NCs are synthesized using oleic acid (OA), oleylamine (OLA) as capping agent and S-ODE as sulfur source.

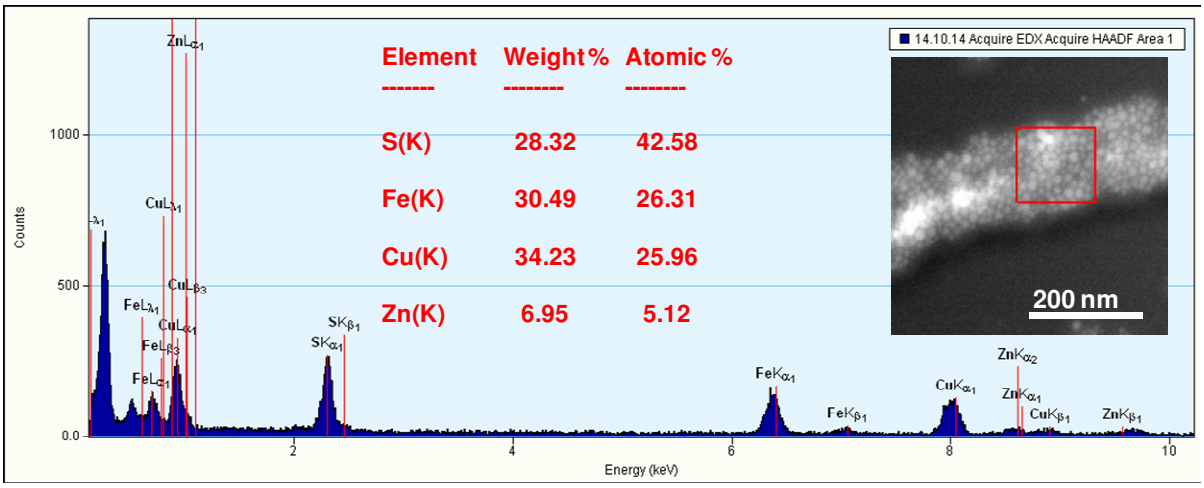


Figure S2. Enegy-despersive x-ray spectrum (EDX) of the CZIS NCs capped with OA and OLA which is showing the spectrum of the constituent elements copper, zinc, iron and sulfur. Right inset is the STEM-HAADF image of the CZIS NCs in which red square area indicates the region from where the EDX spectrum is taken. Middle inset text describes the quantitative analysis of elements present within the CZIS NCs.

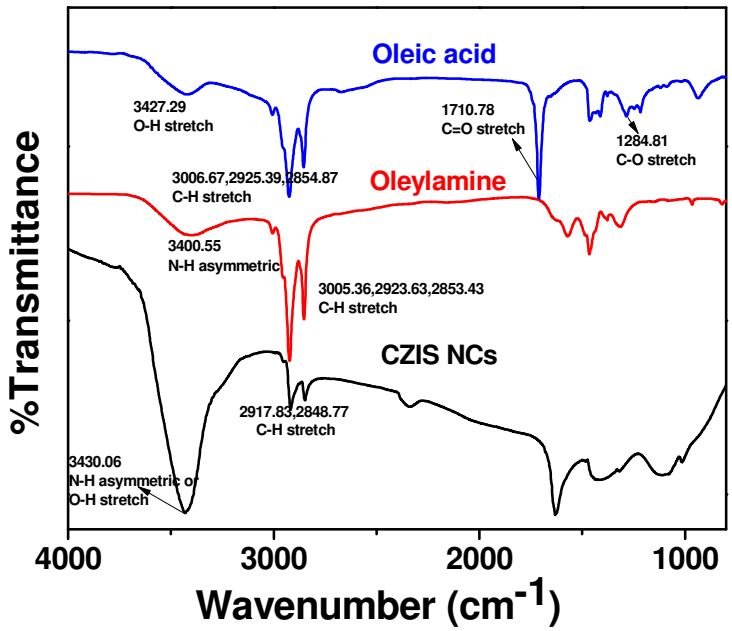


Figure S3. Comparison of the FTIR spectrum of the oleic acid, oleylamine and CZIS NCs synthesized using oleic acid and oleylamine as capping agent.

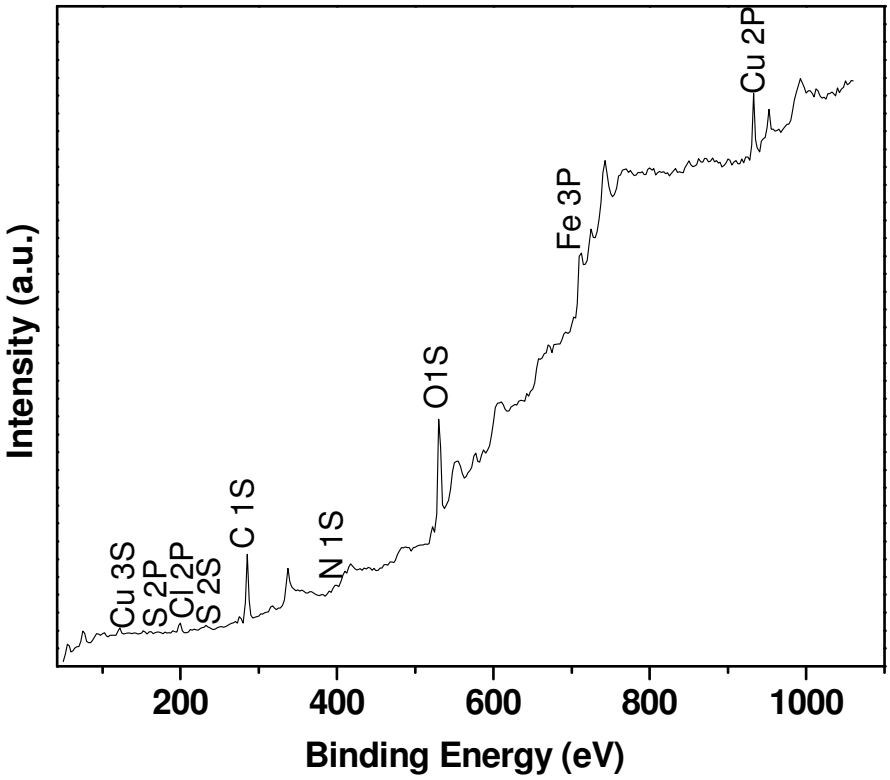


Figure S4. Full range X-ray photoelectron spectrum (XPS) of the CZIS NCs which is showing the binding energy of the elements presents in the CZIS NCs.

Table S1. Atomic percentages (obtained from EDX measurements) of the elements present within the CZIS NCs which are synthesized at different reaction temperature.EDX spectrum have been taken from the thin film of the sample using scanning electron microscope (SEM).

Sample	Atom %				Ratio
CZIS-150	Cu	Zn	Fe	S	Cu : Zn : Fe : S
	24.63	14.73	16.36	44.28	1.67 : 1 : 1.1 : 3
CZIS-200	19.88	15.54	16.82	47.77	1.27 : 1 : 1.08 : 3.07
CZIS-250	23.81	5.06	21.96	49.17	4.7 : 1 : 4.3 : 9.7

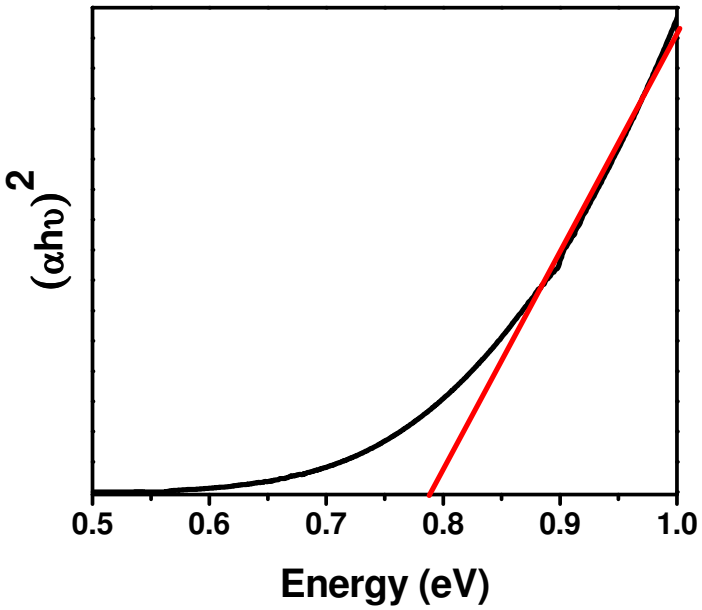


Figure S5. Tauc plot of the CZIS NCs synthesized at temperature 200^{0}C using oleic acid and oleylamine as capping agent. From the Tauc plot, we have obtained a band gap threshold of 0.8 eV.

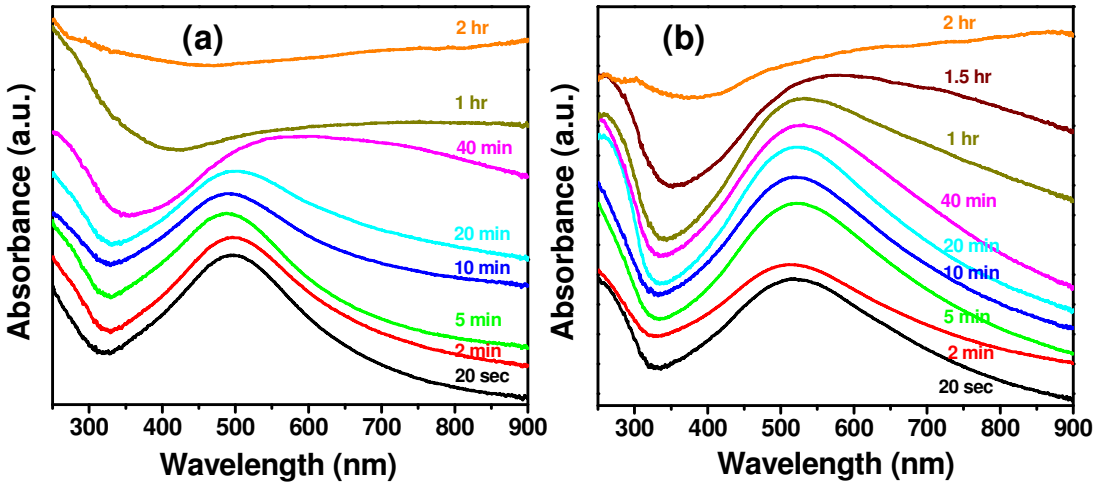


Figure S6. Evolution of UV-vis absorption spectrums of CZIS NCs during annealing time variations at the temperature (a) 200^{0}C and (b) 250^{0}C respectively. Here CZIS NCs are synthesized using oleic acid and oleylamine as capping agent and S-ODE as sulfur source.

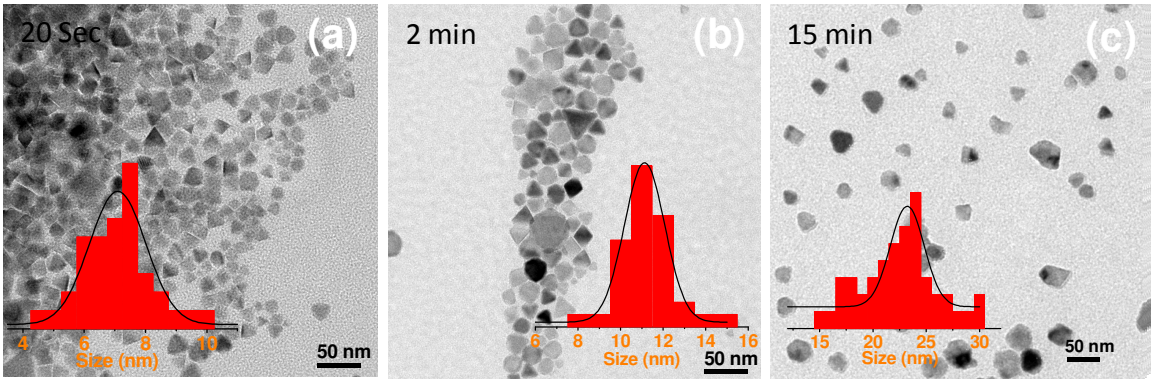


Figure S7. (a-c) TEM images of the CZIS NCs obtained at different annealing time at reaction temperature 250^{0}C. Insets are showing the size distribution of the as obtained CZIS NCs capped with oleic acid and oleylamine.

Table S2. Elemental composition of the CZIS NCs analyzed using ICP-AES at different annealing time at 200^{0}C.CZIS NCs were obtained by taking aliquot at different annealing time and purified before ICP-AES analysis.

Annealing time	Cu Conc. mol/L	Zn Conc. mol/L	Fe Conc. mol/L	Zn/Cu Ratio	Zn/Fe Ratio	Cu/Fe Ratio
20 sec	18.1	5.73	17.7	0.316	0.323	1.02
2 min	17.98	6.62	20.77	0.368	0.318	0.865
5 min	5.1	2.86	5.69	0.56	0.502	0.896
10 min	10.82	3.16	12.06	0.292	0.262	0.897
20 min	17.92	5.55	18.99	0.309	0.292	0.943
40 min	18.84	6.59	18.58	0.349	0.3540	1.01
60 min	33.54	16.29	32.66	0.485	0.498	1.02
120 min	14.07	15.4	12.84	1.09	1.19	1.09

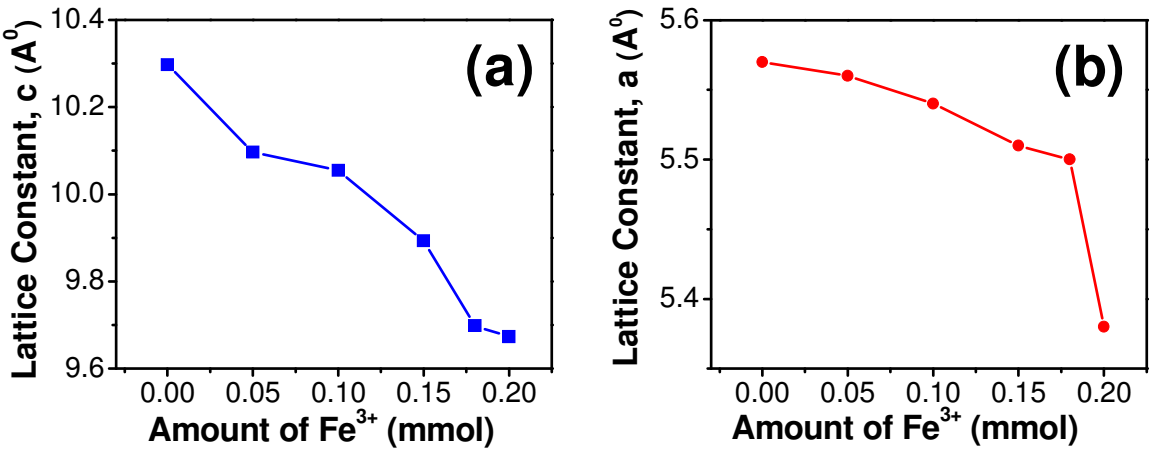
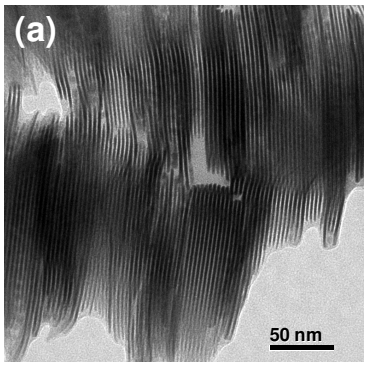
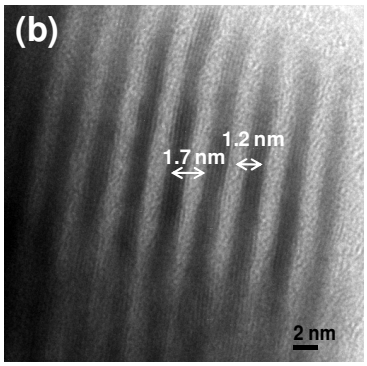


Figure S8. (a-b) Change of lattice constant due to variation of composition of iron and zinc ratio in the composition tunable CZIS NCs.





(c) Sample Name	Cu Conc. mg/L	Zn Conc. mg/L	Fe Conc. mg/L
CZIS-wire	71.28	0.061	0.252

Figure S9. (a) Low resolution TEM images of CZIS nanowires (NWs), (b) high resolution TEM images of CZIS NWs showing the diameter of ~1.2 nm and inter-wire distance of around 1.7 nm.(c) Elemental composition of the CZIS NWs obtained from ICP-AES analysis.

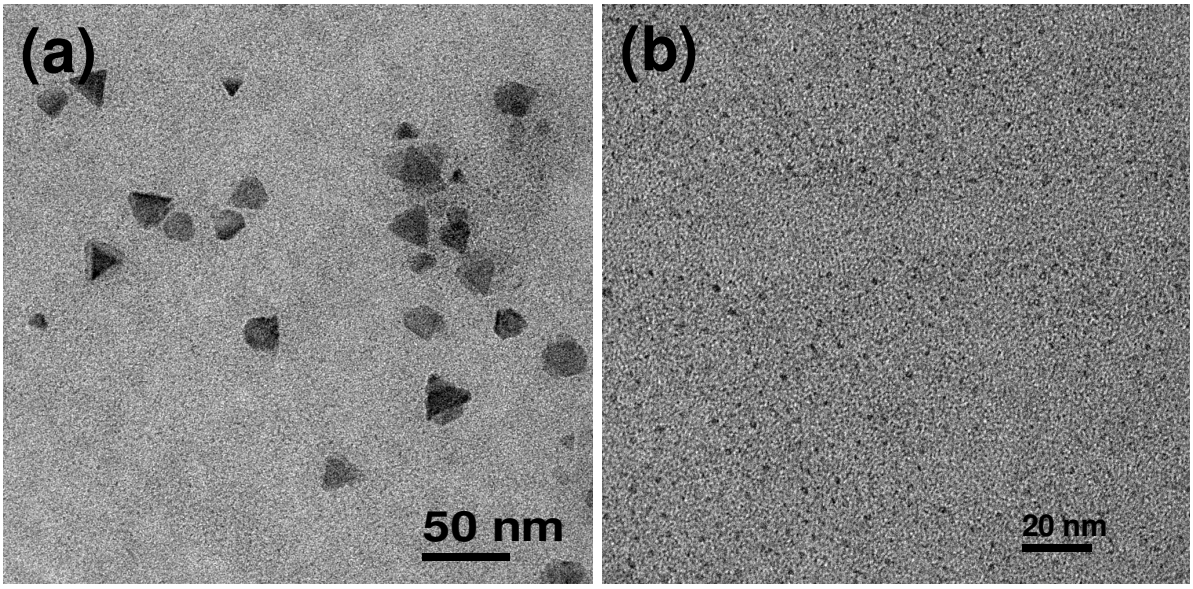


Figure S10. (a-b) TEM images of the CZIS NCs that were obtained using TDPA and oleylamine as capping agent and S-ODE as sulfur source.

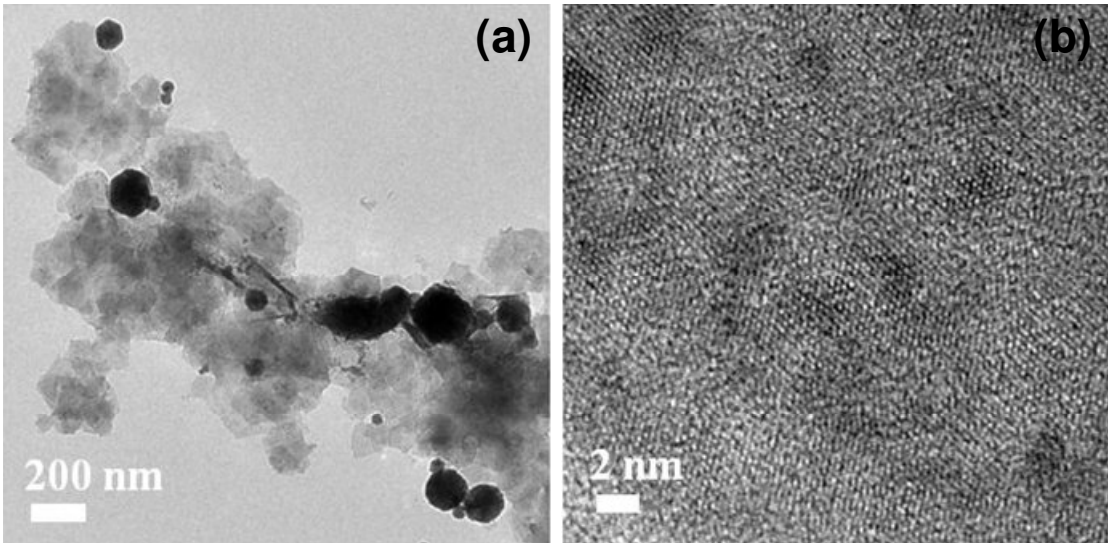


Figure S11. (a) TEM image of the CZIS nanosheets, (b) HRTEM of the CZIS nanosheet which is showing the well resolve lattice planes. Here oleic acid was used as capping agent and 1-DDT as sulfur source.

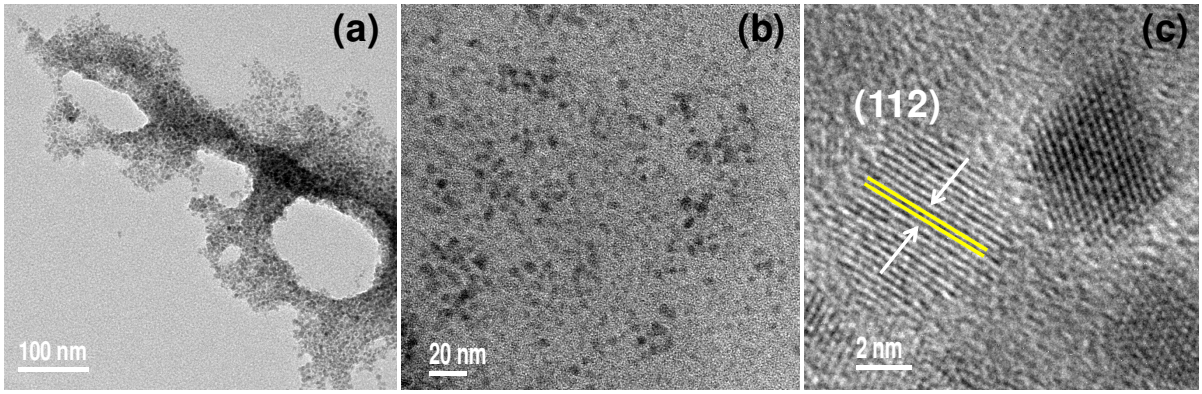


Figure S12.TEM images of the CZIS NCs that was obtained using TDPA as capping agent and TMS as sulfur precursor where (a-b) low resolution TEM and (c) high resolution TEM images which is showing the well resolved interplanar lattice distance corresponding to the (112) plane of the chalcopyrite crystal structures (JCPDS#370471).

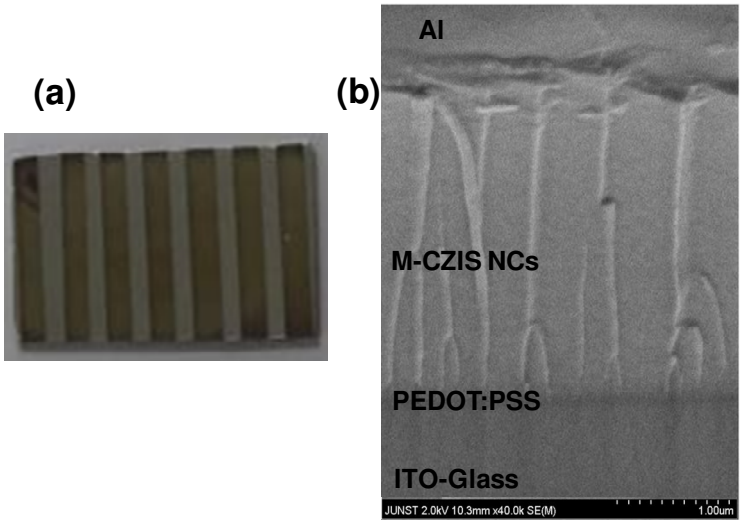


Figure S13. (a) Photograph of a device used for the photoresponse measurement. The device consists of the different active layers ITO-Glass/PEDOT:PSS/M-CZIS NCs/Al. (b) Cross-sectional scanning electron microscope (SEM) image of the shown in (a) indicating the presence of the different active components within the device.

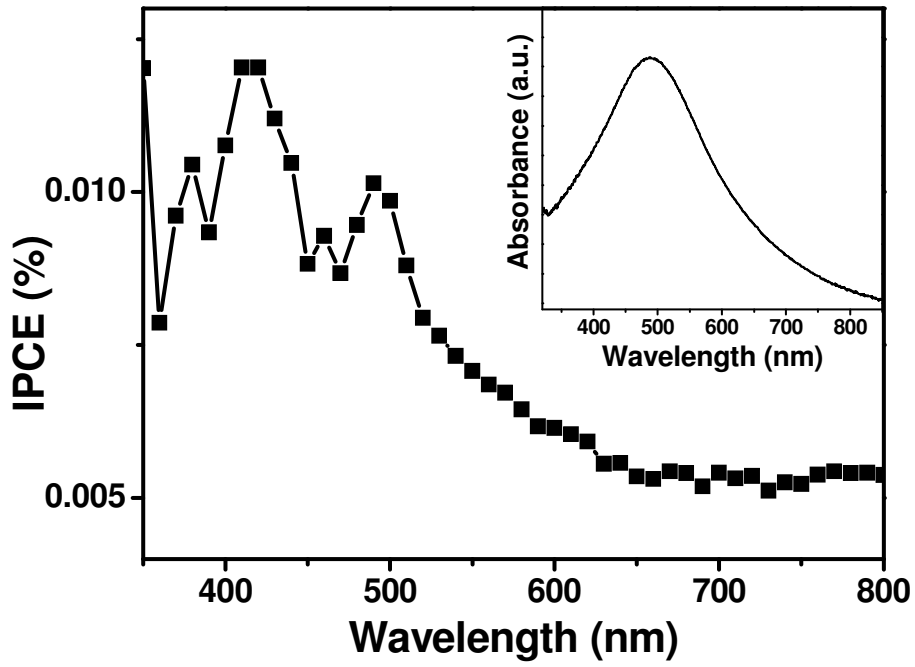


Figure S14. Incident photon-to-current efficiency action spectrum of the device (ITO/PEDOT:PSS/M-CZIS NCs/Al) to check the wavelength dependent photosensitivity of the NCs. Inset of the figure shows the UV-vis absorption spectrum of the thin film of M-CZIS NCs. IPCE spectrum response is similar to that of absorption spectrum NCs indicating that M-CZIS NCs is acting as active component to convert photon into current.

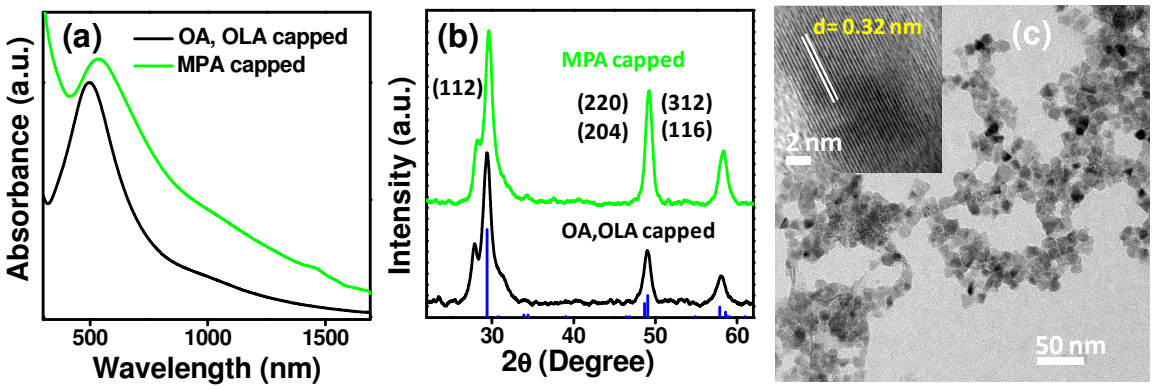


Figure S15. (a) Comparison of UV-vis-NIR absorption spectrums of CZIS NCs capped with oleic acid, oleylamine (OA, OLA) and 3-mercaptopropanoic acid (MPA). Absorption spectrums were taken in tetrachloroethylene as solvent for OA, OLA capped NCs whereas ethanol was used as solvent for MPA capped NCs.(b) Comparison of XRD pattern which are compared with standard JCPDS data file (blue

vertical line) and lattice planes have indexed accordingly.(c) TEM images of MPA capped CZIS NCs where inset is showing the HRTEM image of single CZIS NCs with well resolved lattice planes and the d-spacing corresponds to the (112) plane of chalcopyrite crystal structure.

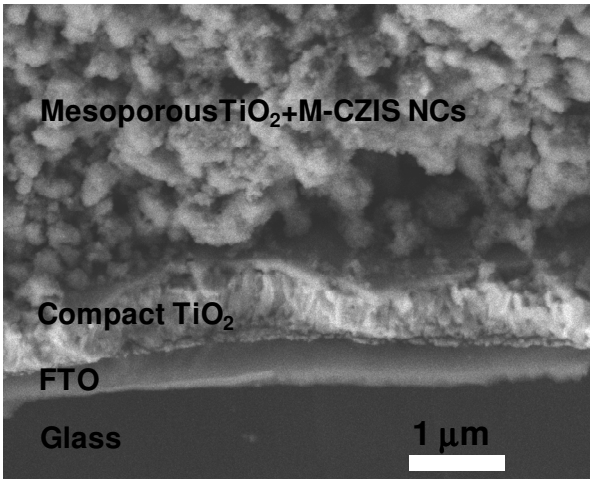


Figure S16. Cross-sectional SEM image of a photoanode sensitized with M-CZIS NCs used for the measurement of quantum dot sensitized solar cell (QDSSCs). SEM image is showing the different active components within the photoanode involve in the QDSSCs.