

Synthesis of CuInS₂-ZnS Alloyed Nanocubes with High Luminescence

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Materials

Copper (II) Acetate (Cu(Ac)₂, ≥98%), Oleic Acid (99.0%), Trioctylphosphine (TOP, 90%), Technical grade 1-Octadecene (ODE, 90%), Indium (III) Acetate (In(Ac)₃, 99.99%), Oleylamine (OA, 70%), 1-Dodecanethiol (DDT, ≥98%) and technical grade Zinc stearate were purchased from Sigma-Aldrich. Chloroform (99.99%) was purchased from Fisher Scientific. All the chemicals were used as received.

Synthesis of CuInS₂-ZnS Nanocrystals

CuInS₂ nanocrystals were prepared by thermal decomposition of a mixture of 0.1mM (18.2mg) of CuAc, 0.1mM (29.2mg) of In(Ac)₃ and 5mM (1.2mL) of r n-dodecylthiol in a 100mL three-necked bottle with 4mL of ODE, 0.2mM (56.4mg) of Oleic Acid and about 0.1mL of TOP. The reaction mixture was heated to the temperature of 120°C under nitrogen atmosphere with magnetic stirring. After 10minutes, ~2mL of aliquot was extracted to confirm the formation of CuInS₂ nanoparticles. At 120 °C, 0.15mM of Zinc Stearate that dissolved in 0.8mL/0.2mL (in a 4:1 ratio) of ODE/Oleylamine (at ~120°C) was drop by drop added into the bottle quickly. The amount of the injected zinc stearate solution was varied to 0.25 mM and 0.35 mM in order to obtain CuInS₂-ZnS nanocubes with different Zn contents. Following this, the mixture was further heated to 210°C and kept at that temperature for 30 minutes to allow the diffusion of Zn in CuInS₂ and the growth of CuInS₂-ZnS alloyed nanocrystals. The obtained nanoparticles were firstly washed using absolute ethanol so as to remove unreacted precursors, and the washing process was repeated 3 times. The purified nanoparticles were then dispersed in toluene for storage.

Phase Transfer of the hydrophobic CuInS₂-ZnS nanocubes

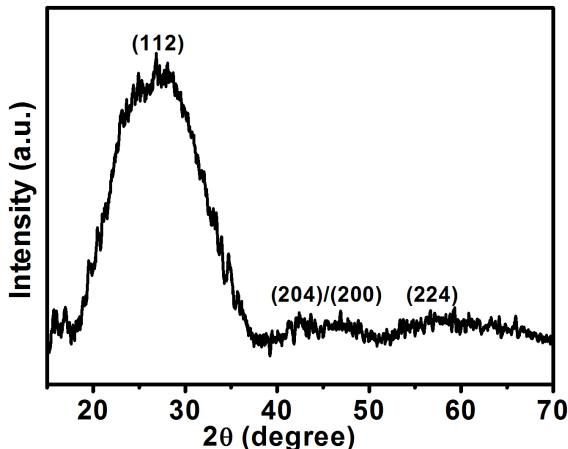
The hydrophobic CuInS₂-ZnS nanocubes were phase-transferred to water using alkylamine grafted poly(isobutylene-*alt*-maleic anhydride) amphiphilic polymer. To achieve highly dispersed hydrophilic nanoparticles, a large polymer/nanoparticle ratio was used to avoid the aggregation. In a typical process, CuInS₂-ZnS nanocubes(5 mg) and the polymer (25 mg) were dispersed in chloroform (1 mL). The solvent was evaporated and then dried in vacuum for 2 days to obtain a completely dried nanoparticle/polymer composite. The dried composite could be re-dissolved in water (5 mL) to form stable colloids. The nanoparticles were purified by dialyzing against Millipore water for 3 days in a dialysis sac (molecular weight cut-off=12 kDa).

Cellular labelling with CuInS₂-ZnS nanocubes

NIH/3T3 and OCA17 cells were seeded in a 96-well plate, incubated at 37°C, at pH 7.4, in a humidified and 5% CO₂ atmosphere. After 24 hours, 10 µL of the water-dispersed CuInS₂-ZnS nanocubes with a concentration of 10 µg/mL were injected into each well. With the nanocrystals added, the cells were incubated for another 24 hours at the same conditions. A control for the cells was also prepared with the same conditions without the nanocrystals added. After incubation, images were taken using a Confocal laser scanning microscopy, Olympus Fluoview FV300 equipped with a Chameleon-XR laser (Ti:Sapphire femtosecond laser) at the tuning range of 760-920nm for 2-photon bioimaging as well as a Olympus Ix2-DSU disk scanning confocal microscope for UV cell imaging.

Characterization

Powder X-ray diffraction (XRD) was carried out on a D8 Advance Bruker-AXS (GmbH, Karlsruhe, Germany). The X-ray source used was Cu K α (1.5405 Å) (40kV, 200mA); the powder samples were prepared by drying the purified product at room temperature on a glass slip. Photoluminescence (PL) spectra were measured using a LS 55 Perkin-Elmer Luminescence Spectrometer. The PL quantum yields of the samples were determined and calculated using the cross-calibrated method mentioned in Deng et al. by referencing to Rhodamine 101 (QY=100% in ethanol + 0.01 HCl) for red emissions and Rhodamine 110 (QY=90% in ethanol) for yellow and orange emissions. UV-Visible absorption spectra were recorded by a Varian Cary 5000 UV-Vis-NIR Spectrophotometer. Transmission Electron Microscope (TEM), high-resolution transmission electron Microscope (HRTEM) images and Energy Dispersive Spectroscopy (EDS) were obtained using JEOL JEM-2010F and JEOL JEM-3010F Field Emission TEM operating at 200kV and 300kV respectively. Samples for the TEM were prepared by depositing a drop of the samples dispersed in toluene onto a carbon coated copper grid and drying at room temperature. The compositions of the nanocrystals were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using Perkin-Elmer Dual-view Optima 5300 DV ICP-OES system. Two-photon Fluorescence (TPF) was measured using a femtosecond Ti: sapphire oscillator from Spectra-Physics (Tsunami). The Ti:sapphire laser generates pulses with a pulse width of about 130fs at 800nm.

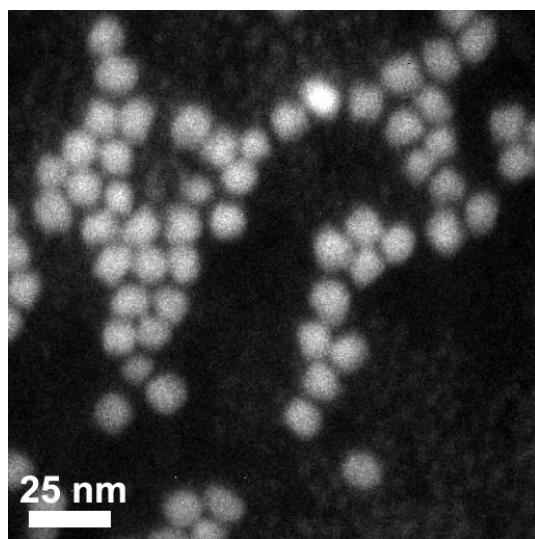


S_Fig. 1 XRD pattern of CuInS₂ seeds formed at 120 oC. (Tetragonal CuInS₂, JCPDS card No. 85-1575)

Sample	Element	Weight (ppm)	#Moles (10 ⁻³)	Cu:In:Zn ratio
1	Cu	0.11	1.731	1:1.057:1.237
	In	0.21	1.829	
	Zn	0.14	2.141	
2	Cu	0.17	2.680	1:1.009:2.185
	In	0.31	2.7	
	Zn	0.38	5.85	
3	Cu	0.12	1.89	1:0.9687:3.17
	In	0.21	1.83	
	Zn	0.39	6.00	

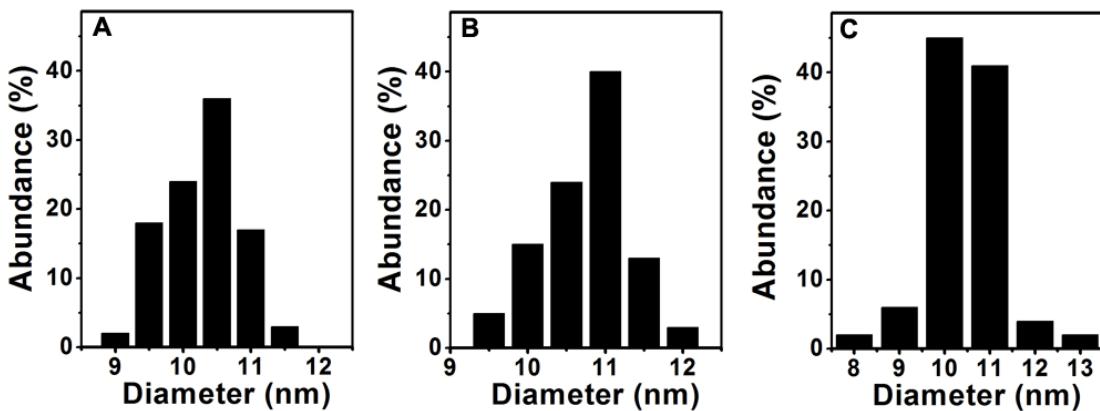
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S_Table 1 Elemental Analysis of the CuInS₂-ZnS nanocubes by ICP-OES.

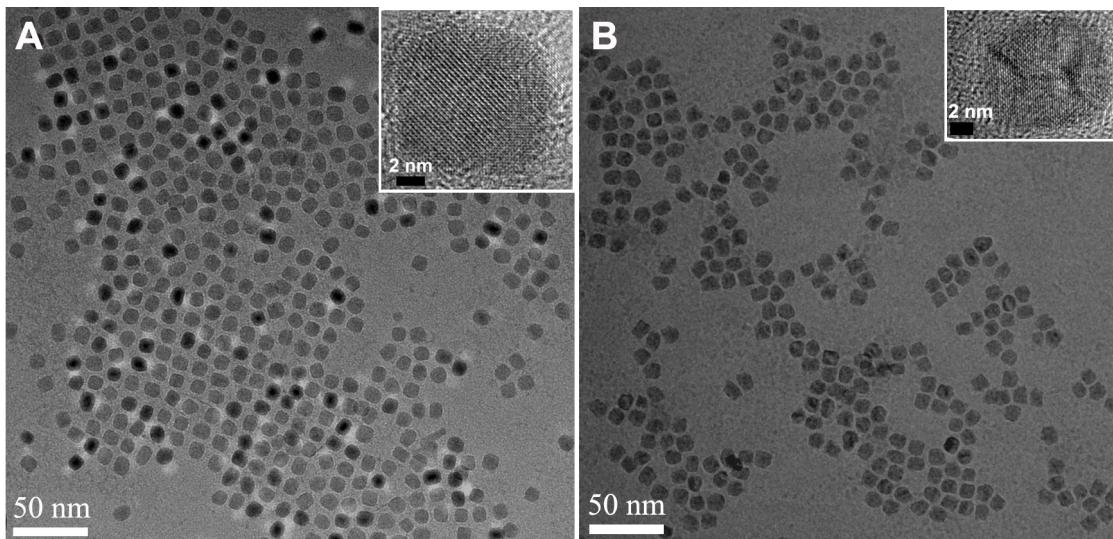


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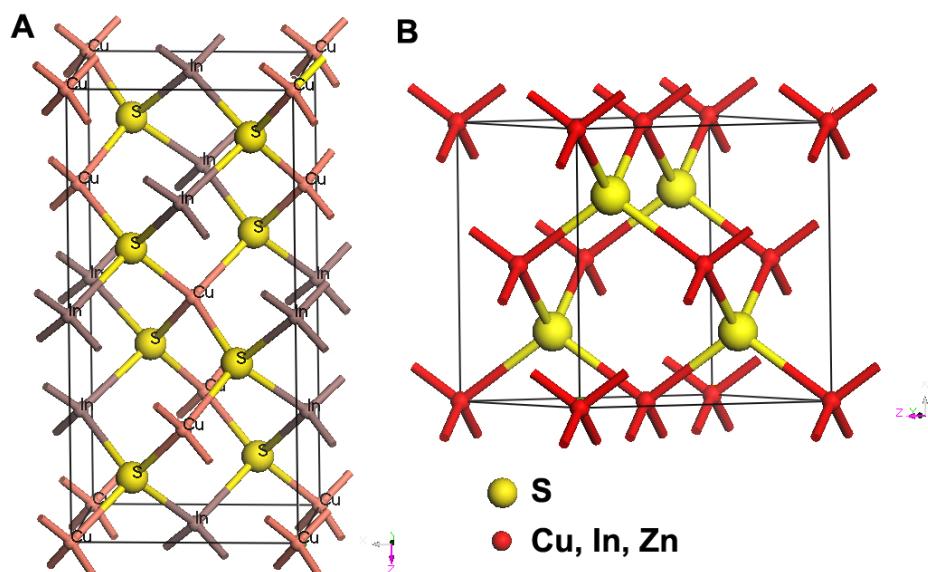
S-Fig.2. EFTEM image of CuInS₂-ZnS alloyed nanoparticles showing the element distribution of Zinc.



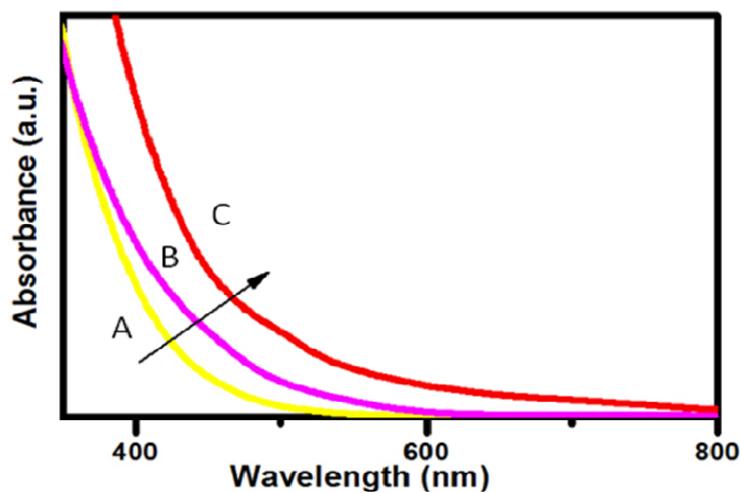
S_Fig.3 Histograms of size distributions of the CuInS₂-ZnS alloyed nanocubes with different mole fractions of zinc, (A) 62%, (B) 52%,(C) 38%, respectively.



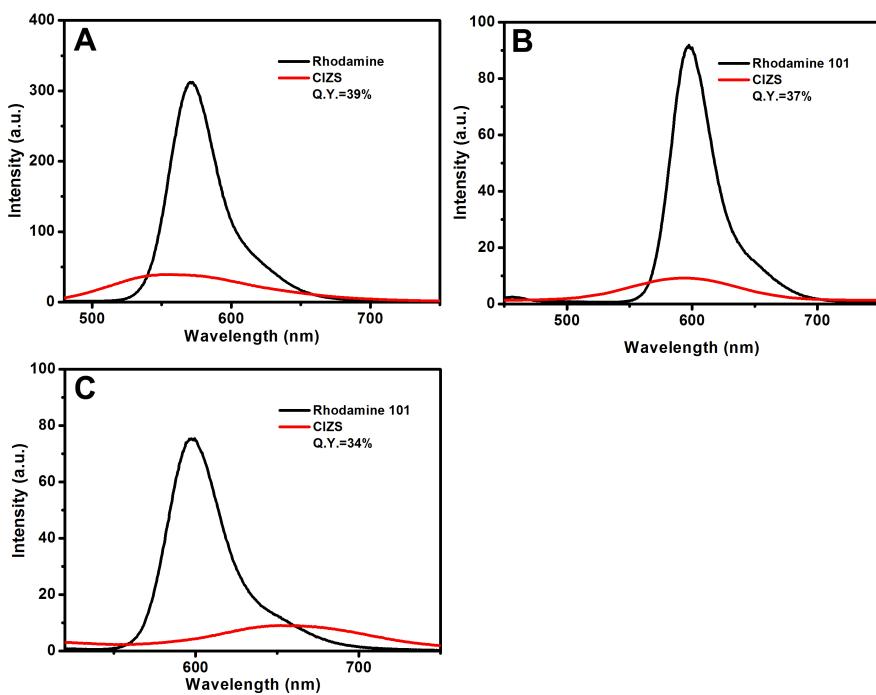
S_Fig.4 TEM images of the CuInS₂-ZnS alloyed nanocubes with zinc mole fractions of (A) 52% and (B) 38%, respectively.



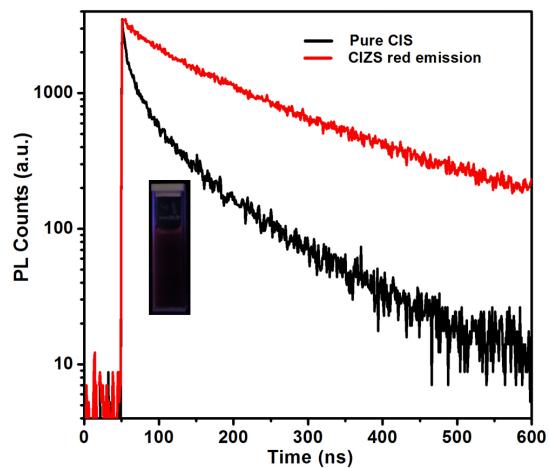
S_Fig.5 (A) Ball and stick model of the crystal structure of CuInS₂(B) the possible crystal structure model of CuInS₂-ZnS, in which Cu and In ions are partially replaced with Zn ions.



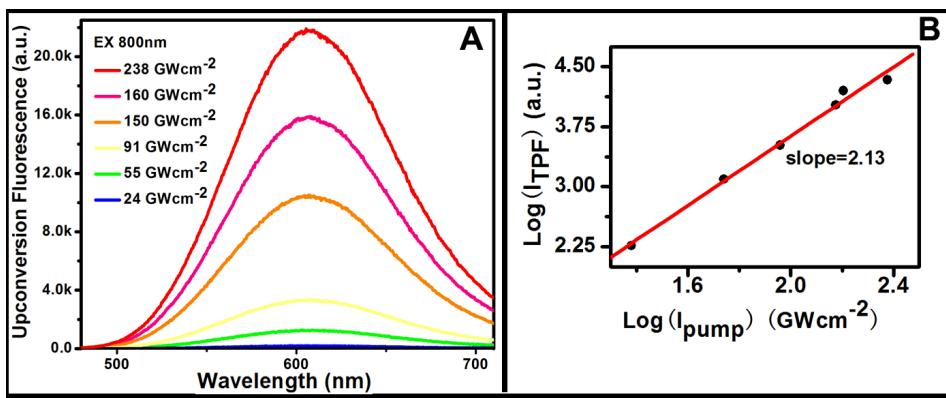
S_Fig. 6 The absorption spectra of the CuInS₂-ZnS alloyed nanocubes with different zinc mole fractions (A) 62%, (B) 52% and (C) 38%, respectively.



S_Fig.7 PL emission spectra of the CuInS₂-ZnS alloyed nanocubes with zinc mole fractions (A) 62%, (B) 52% and (C) 38 %, respectively, in comparison with the standard rhodamine 6G ethanol solution (QY=95%) or rhodamine 101 ethanol solution (QY=100%). The quantum yields of the nanocubes were (A) 39%, (B) 37% and (C) 34%, respectively.



S_Fig.8 PL relaxation of the nanocubes with zinc mole fraction of 38%, as compared to that of the pure CuInS₂ nanoparticles. Inset is the photograph of pure CIS nanoparticles under UV-365nm lamp.



S_Fig.9 (A) Upconversion emission of the CuInS₂-ZnS alloyed nanoparticles with zinc mole fraction of 52% with various input powers. (B) The corresponding quadratic dependence of integrated fluorescence intensity with the input power of laser, showing that the upconversion mechanism is two-photon.