

## SUPPLEMENTARY INFORMATION

### **Developing a facile method for highly luminescent colloidal CdS<sub>x</sub>Se<sub>1-x</sub> ternary nanoalloys** **Caner Ünlü, Gülçin Ünal Tosun, Seçil Sevim and Serdar Özçelik**

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**Synthesis of Cadmium Myristate:** The cadmium precursor was prepared by following the method given provided by Pan et al (D. C. Pan, S. C. Jiang, L. J. An and B. Z. Jiang, *Advanced Materials*, 2004, 16, 982-985). Typically, 10 mmoles of cadmium oxide (CdO) and 20 mmoles of myristic acid were mixed and heated at 200 °C for ten minutes. The reaction was terminated when a clear solution was obtained. Cadmium myristate (CdMA) was recrystallized with toluene, dried at room temperature and stored at the freezer.

**Synthesis of NaHSe as Se precursor:** NaHSe was synthesized according to previously published procedure (L. Klayman and T. S. Griffin, *Journal of the American Chemical Society*, 1973, 95, 197-200). Se powder (0.4 mmol) and NaBH<sub>4</sub> (1 mmol) were mixed in a 5 ml reaction flask under N<sub>2</sub> atmosphere. Then 1 ml of N<sub>2</sub> saturated distilled water added to the reaction medium by a glass syringe. The solution was allowed to form a white precipitate under the N<sub>2</sub> flow. The resulting clear solution was directly used without any further purification. In all experiments, NaHSe solutions just freshly synthesized were used.

**Synthesis of the ternary CdS<sub>x</sub>Se<sub>1-x</sub> nanoalloys:** The ternary CdS<sub>x</sub>Se<sub>1-x</sub> nanoalloys were synthesized by modifying the two – phase approach in a three – neck flask by using an oil – soluble Cd source, an organic surfactant (dissolved in a non – polar solvent such as toluene), a highly reactive Se source and a S source with a considerably slow reaction rate compared to Se source (in aqueous phase). 0.4 g Cadmium myristate (CdMA) and 2.0 g of oleic acid (OA) or tri-n-octylphosphine oxide (TOPO) was dissolved in 80 ml of toluene in 80 °C in a beaker. Then, the three – necked flask was purged with N<sub>2</sub> to remove O<sub>2</sub> completely from the experiment set-up. Afterwards, NaHSe (varied between 3 mg – 9 mg) and thiourea (varied between 30 mg – 150 mg) were co-dissolved in N<sub>2</sub> saturated water (80 ml) and poured into the three – necked flask. Later, the NaHSe - thiourea mixture heated to 100 °C for 30 minutes under vigorous stirring under N<sub>2</sub> atmosphere. Then, the CdMA and OA (TOPO) dissolved in toluene at 80 °C were swiftly added to the hot aqueous solution of NaHSe and thiourea mixture. The co-existence of Se and S precursors assured the formation of the nanoalloys. The colloidal CdS<sub>x</sub>Se<sub>1-x</sub> nanoalloys begin to form following the injection of the chalcogenide mixture in 15 minutes in toluene.

Aliquots of sample (0.5 ml taken from the growth solution, diluted by 2-3 ml toluene) were taken at different times to monitor the progress of the nanoalloy formation by using UV – vis and fluorescence spectrometers and DLS measurements. The reaction was stopped at a time by cooling the solution to the room temperature when the pre-determined size was reached up. The experimental set-up was under N<sub>2</sub> atmosphere during whole procedure.

**Purification:** The nanoalloys were purified by precipitating the crude solution with the addition of ethanol (50 ml). The mixture was waited overnight under N<sub>2</sub> atmosphere and precipitate was collected afterwards. The purification procedure was repeated several times to remove unreacted species, excess capping agent and surfactants by observing brightness of the samples and measuring the quantum yields.

**Synthesis of the CdS nanocrystals:** The CdS nanocrystals were synthesized by using the two – phase approach in a three – neck flask. 0.4 g Cadmium myristate (CdMA) and 2.0 g of oleic acid (OA) or tri-n-octylphosphine oxide (TOPO) was dissolved in 80 ml of toluene at 80 °C in a flask. Then, the three – necked flask purged with N<sub>2</sub> to remove O<sub>2</sub> completely from experiment the set-up. Afterwards, thiourea (60 mg) was dissolved in N<sub>2</sub> saturated water (80 ml) and poured into the three – necked flask. Later, thiourea solution heated to 100 °C for 30 minutes under vigorous stirring under N<sub>2</sub> atmosphere. Then, the CdMA and OA (TOPO) dissolved in toluene at 80 °C were added to the hot aqueous solution of thiourea. The colloidal CdS nanocrystals begin to form within 60 minutes in toluene. The reaction was stopped at a time by cooling the solution to the room temperature when the pre-determined size was reached up. The experimental set-up was under N<sub>2</sub> atmosphere during the whole procedure. The samples were purified following the procedure given above.

**Synthesis of the CdSe nanocrystals :** The CdSe nanocrystals were synthesized by using the two – phase approach in a three – neck flask by using an oil – soluble Cd source, an organic surfactant (dissolved in a non – polar solvent such as toluene), and a highly reactive Se source. 0.4 g Cadmium myristate (CdMA) and 2.0 g of oleic acid (OA) or tri-n-octylphosphine oxide (TOPO) was dissolved in 80 ml of toluene in 80 °C in a beaker. Then, the three – necked flask purged with N<sub>2</sub> to remove O<sub>2</sub> completely from experiment set-up. Afterwards, NaHSe (3 mg) was dissolved in N<sub>2</sub> saturated water (80 ml) and poured into the three – necked flask. Later, NaHSe solution heated to 100 °C for 30 minutes under vigorous stirring under N<sub>2</sub> atmosphere. Then, the CdMA and OA (TOPO) dissolved in toluene at 80 °C were added to the hot aqueous solution thiourea on a sudden. The colloidal CdSe nanocrystals begin to form within 15 minutes in non – polar solvent. The reaction was stopped at a time by cooling the solution to the room temperature when the pre-determined size was reached up. The experimental set-up was under

N<sub>2</sub> atmosphere for whole procedure. The samples were purified following the procedure given above.

The table provides the real amount of the reactant used in the preparations.

Cd:Se:S	Cd – MA (mg)	NaHSe (mg)	Thiourea (mg)	TOPO (gr)	OA (gr)	Reaction Time (hours)	Composition
8 : 1 : 7	400	9	60	2	-	5	CdS <sub>0.17</sub> Se <sub>0.83</sub>
12 : 1 : 11	400	6	60	2	-	5	CdS <sub>0.50</sub> Se <sub>0.50</sub>
24 : 1 : 22	400	3	60	2	-	5	CdS <sub>0.75</sub> Se <sub>0.25</sub>
24 : 1 : 33	400	3	90	2	-	5	CdS <sub>0.92</sub> Se <sub>0.08</sub>
24 : 1 : 55	400	3	150	2	-	5	CdS <sub>0.95</sub> Se <sub>0.05</sub>
24 : 0 : 22	400	-	60	2	-	5	CdS
24 : 1 : 0	400	3	-	2	-	5	CdSe

Compositions were determined by XRD obtained at the end of the reaction.

### Optical Characterization

All absorption data were obtained by Varian Cary 50 UV-Vis spectrometer, and fluorescence data were obtained by Varian Cary Eclipse fluorescence spectrometer. The optical density of nanocrystals was at most 0.1 (for the 0 → 1 transition peak) to prevent any distortion caused by self absorption. For emission spectra, the samples were excited at 350 nm. All samples are purified and dissolved in toluene, except for time – growth spectra, in which the crude solutions that taken directly from growth medium were used.

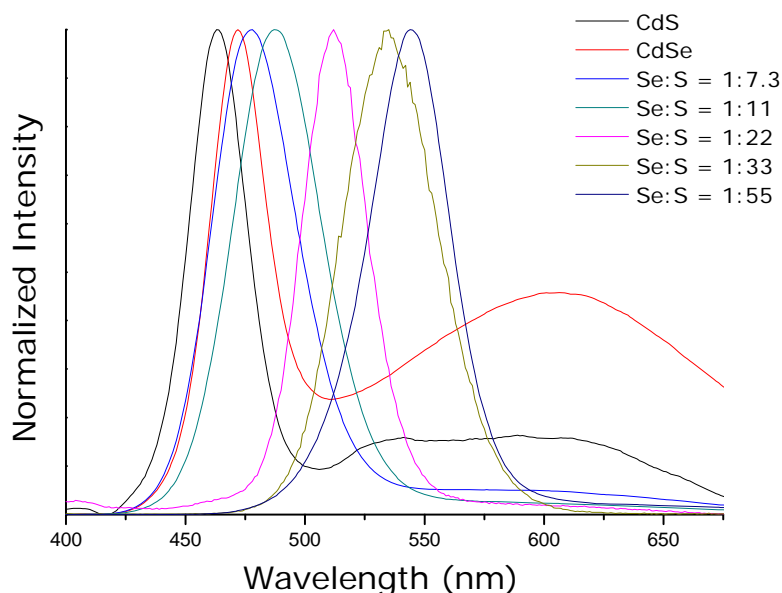


Figure S1. Fluorescence spectra of TOPO capped CdS<sub>x</sub>Se<sub>1-x</sub> with different fractions of Se:S incorporated. The CdS and CdSe at the same size of the nanoalloys are provided for comparison.

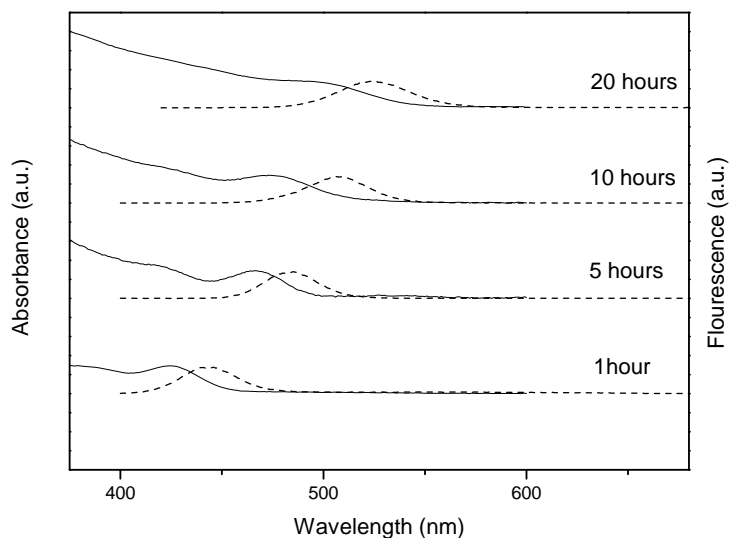


Figure S2. Absorption and emission spectra of  $\text{CdS}_{0.75}\text{Se}_{0.25}$  nanoalloys capped by oleic acid, grown at various reaction times: 1 – 20 hours.

### Structural characterization:

#### XRD:

XRD measurements were carried out with Panalytical X'Pert Pro Materials Research Diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). The XRD data was collected in step scanning mode in the range from  $10^\circ$  to  $60^\circ$ . The purified and completely dried samples (dried under nitrogen atmosphere) were used in data collection.

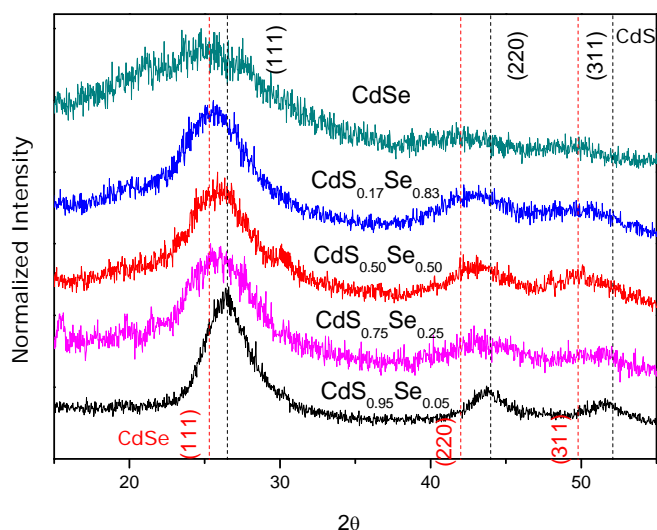


Figure S3. XRD diffractogram of the  $\text{CdS}_x\text{Se}_{1-x}$  nanoalloys synthesized with different initial Se:S ratios. The Vegard's law was used for the determination of the fractions of Se and S.

## EDX:

EDX data were collected with Philips XL 30S FEG Scanning Electron Microscope (for samples 1:7, 1:11 and 1:22 Se:S experimental starting ratios) and a Zeiss 912 Omega microscope working at a voltage of 120 kV or a Technai F20 microscope working at a voltage of 200 kV SFEG (for sample 1:55 Se:S experimental starting ratio ) for the elemental analysis. The purified and completely dried samples (dried under nitrogen atmosphere) were analyzed.

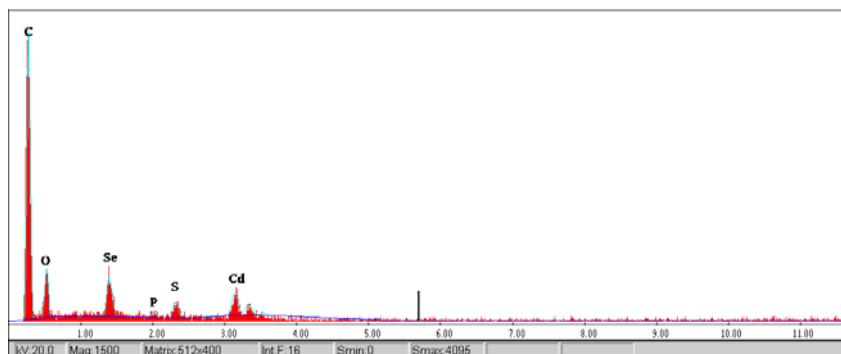


Figure S4. SEM - EDX spectrum of  $\text{CdS}_x\text{Se}_{1-x}$  with Se:S = 1:7 starting ratio. Obtained data confirms that the structure of nanoalloy is  $\text{CdS}_{0.24}\text{Se}_{0.76}$

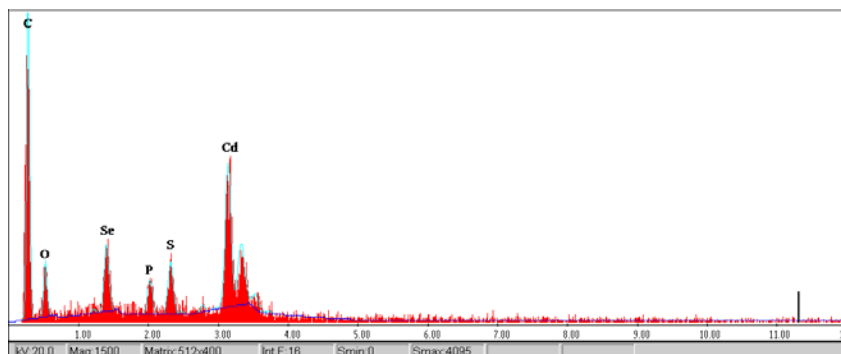


Figure S5. SEM - EDX spectrum of  $\text{CdS}_x\text{Se}_{1-x}$  with Se:S = 1:11 starting ratio. Obtained data confirms that the structure of nanoalloy is  $\text{CdS}_{0.50}\text{Se}_{0.50}$

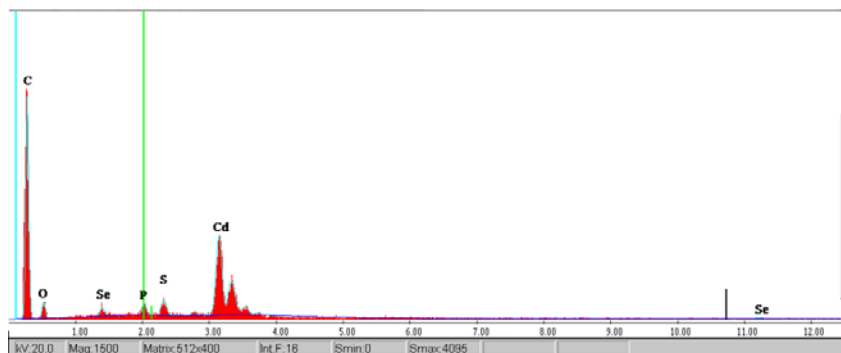


Figure S6. SEM - EDX spectrum of  $\text{CdS}_x\text{Se}_{1-x}$  with Se:S = 1:22 starting ratio. Obtained data confirms that the structure of nanoalloy is  $\text{CdS}_{0.75}\text{Se}_{0.25}$

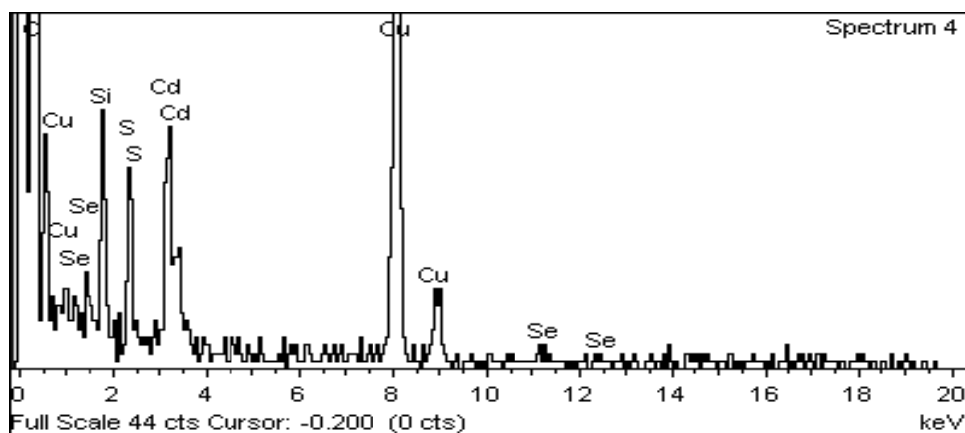


Figure S7. TEM - EDX spectrum of  $\text{CdS}_x\text{Se}_{1-x}$  with Se:S = 1:55 starting ratio. Obtained data confirms that the structure of nanoalloy is  $\text{CdS}_{0.94}\text{Se}_{0.06}$

We monitored **the change in the nanoalloy composition as a function of growth time**, by EDX spectra. These spectra were given below, and used to construct Fig. 5 in the main text.

Fig S8a. EDX spectra at 1 hour, for the nanoalloy  $\text{CdS}_{0.75}\text{Se}_{0.25}$

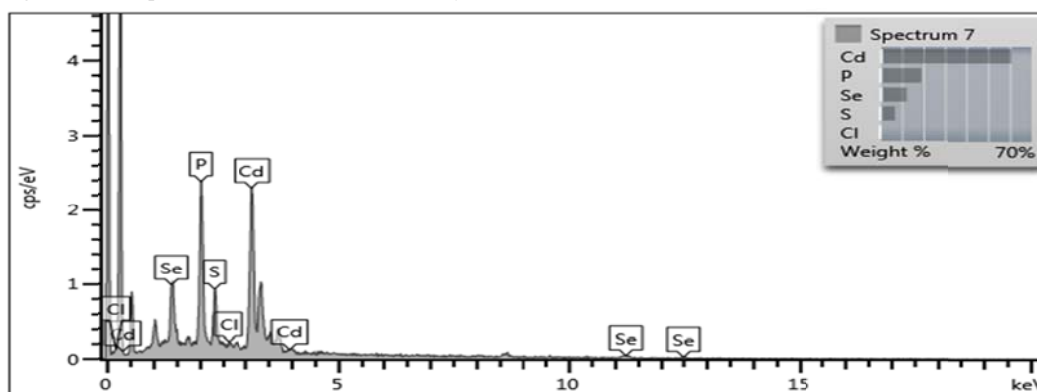


Fig S8b. EDX spectra at 2 hours, for the nanoalloy  $\text{CdS}_{0.75}\text{Se}_{0.25}$

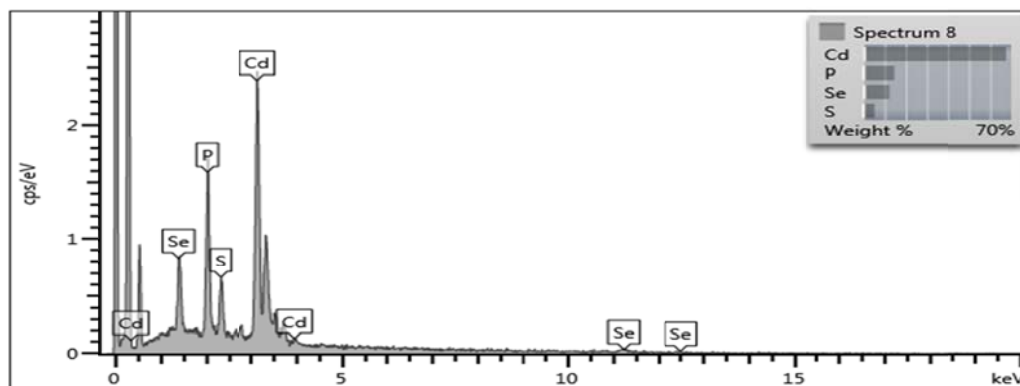


Fig 8Sc. EDX spectra at 3 hours, for the nanoalloy  $\text{CdS}_{0.75}\text{Se}_{0.25}$

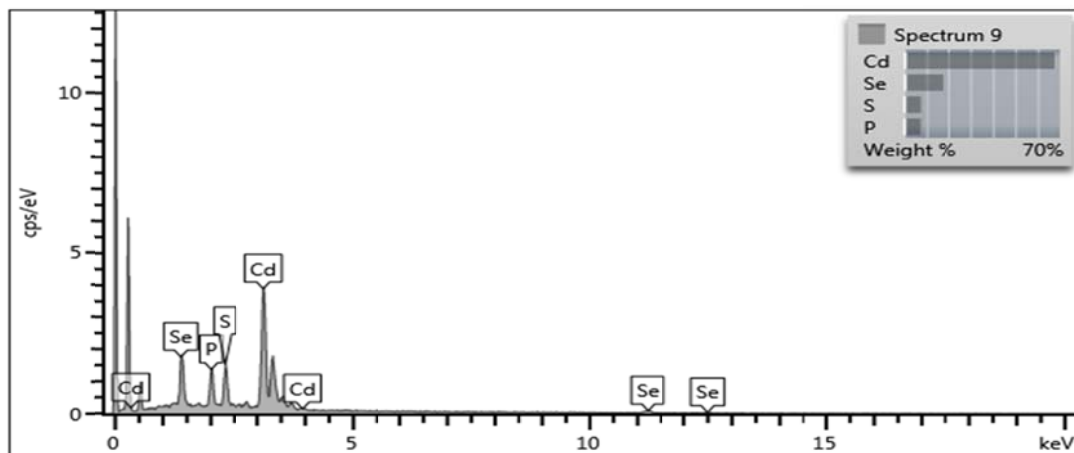


Fig 8Sd. EDX spectra at 4 hours, for the nanoalloy  $\text{CdS}_{0.75}\text{Se}_{0.25}$

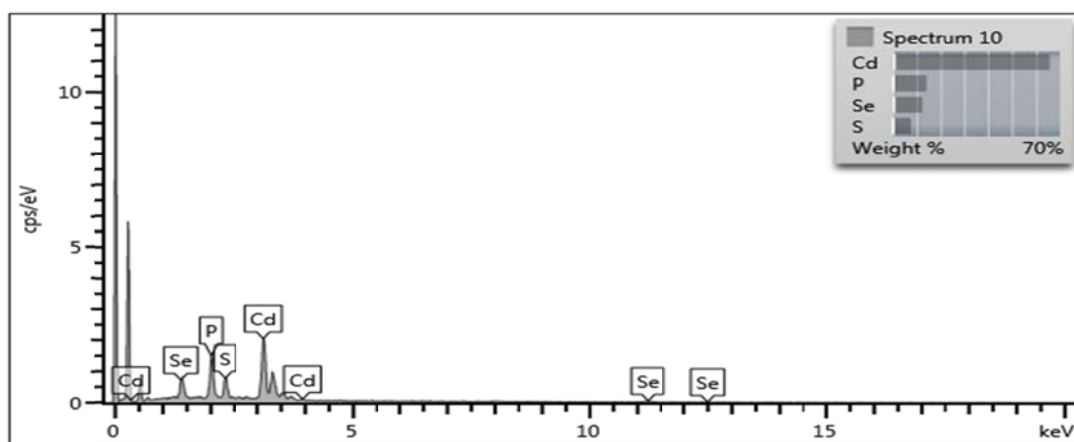


Fig 8Se. EDX spectra at 5 hours, for the nanoalloy  $\text{CdS}_{0.75}\text{Se}_{0.25}$

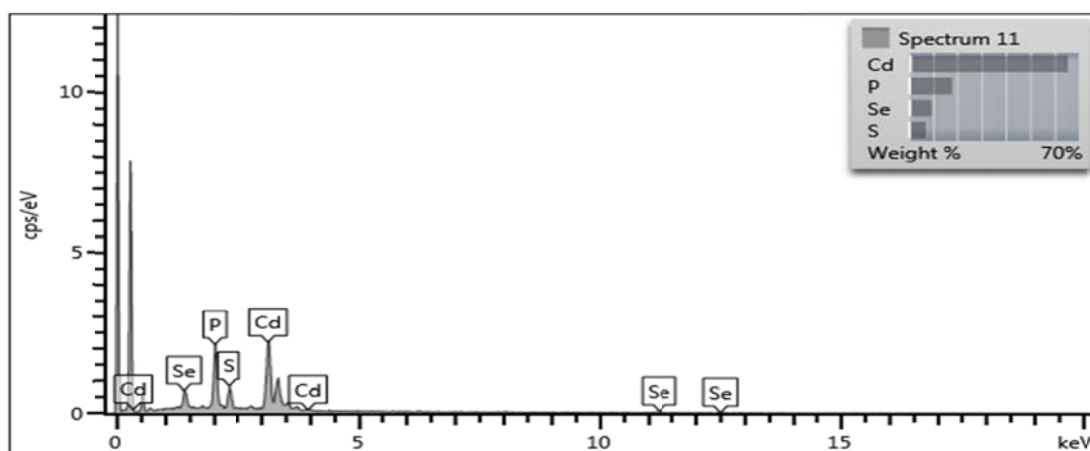


Fig 8Sf. EDX spectra at 7 hours, for the nanoalloy  $\text{CdS}_{0.75}\text{Se}_{0.25}$

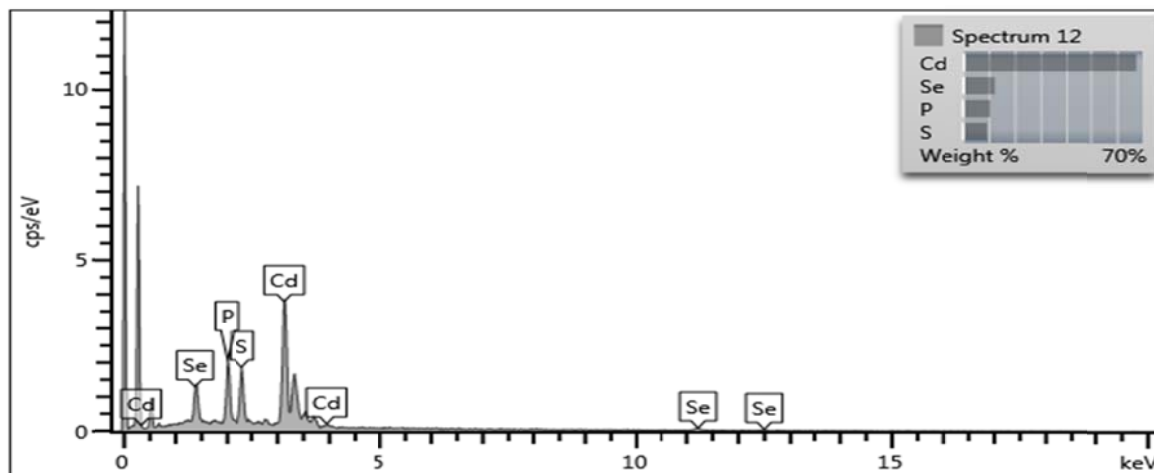
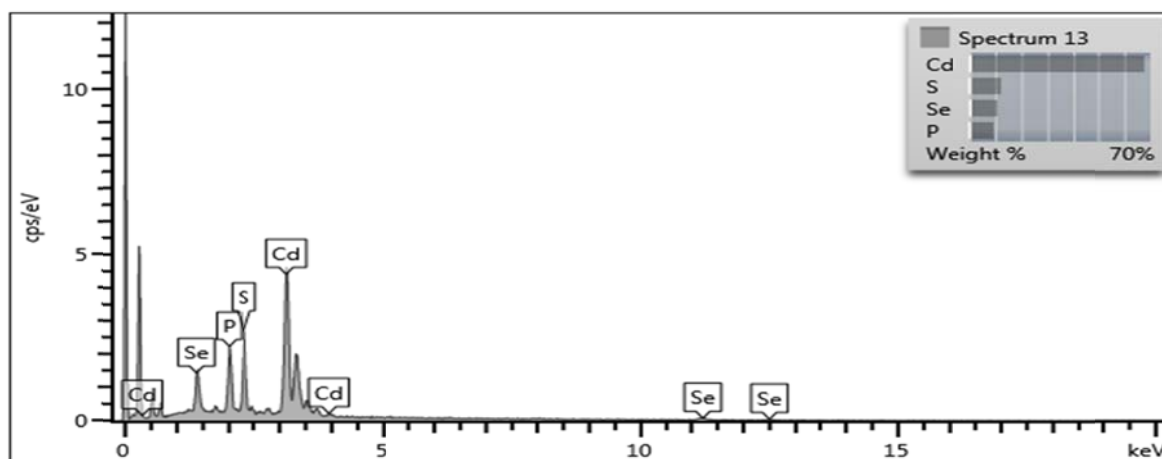


Fig 8Sg. EDX spectra at 10 hours, for the nanoalloy  $\text{CdS}_{0.75}\text{Se}_{0.25}$



**The DLS data for representing the hydrodynamic diameter.**

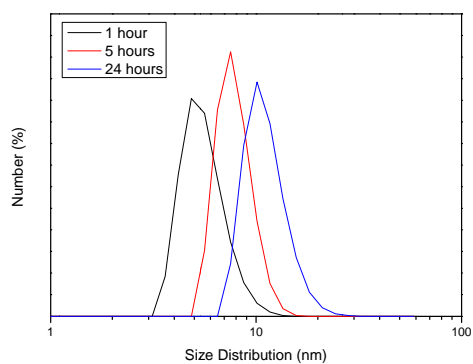


Figure S9. DLS data for the size-controlled nanoalloys.



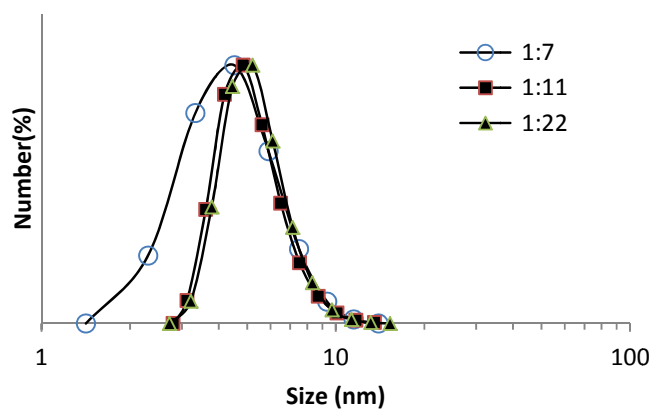


Figure S10. DLS data for the composition-controlled nanoalloys.

TEM:

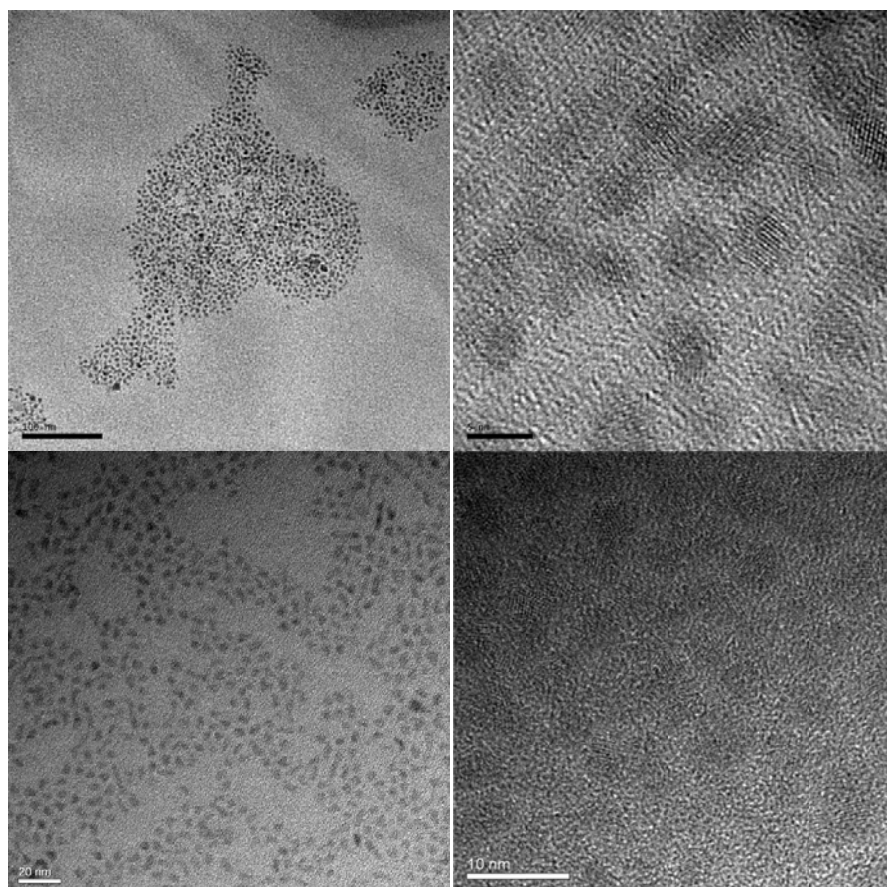


Figure S11. TEM and HRTEM images of the nanoalloys.

### Demonstration of Biomedical / Biological Application of the nanoalloys

This part of the supplementary information provides a demonstration of a biomedical / biological application of the nanoalloy  $\text{CdS}_{0.75}\text{Se}_{0.25}$  capped with mercaptopropionic acid in live cell imaging. In this study, A549 human adenocarcinoma lung cells were incubated with  $\text{CdS}_{0.75}\text{Se}_{0.25}$  nanoalloys with a concentration of  $1 \mu\text{g/mL}$  for one hour. A sequence of 100 frames were captured with the exposure time of 100 ms. A spinning disc confocal microscope (ANDOR Revolution) was used for tracking the motion and location of the nanoalloys in live cell conditions. In Figure A, the nanoalloys appear as green fluorescent spots in the cellular environment of the A549 cells. From the Figure B, it was clearly seen that photobleaching did not occur in the observation period. In each frame, we have position information in both x and y directions of the emitting spot that corresponds to a “single particle”. By analyzing individual positions in each frame we created trajectories of the nanoalloys. The spot analysis per frame helped us to generate the trajectories of the nanoalloys. In Figure C, it was obvious that the nanoalloys diffuse randomly in A549 cells. We estimate the diffusion coefficient through MSD analysis and the type of diffusion undergone by the particle. As it is seen in Figure D, the slope of the MSD versus time plot is nearly constant in the observation period. This figure shows the random motion of the nanoalloys on the cellular environment.

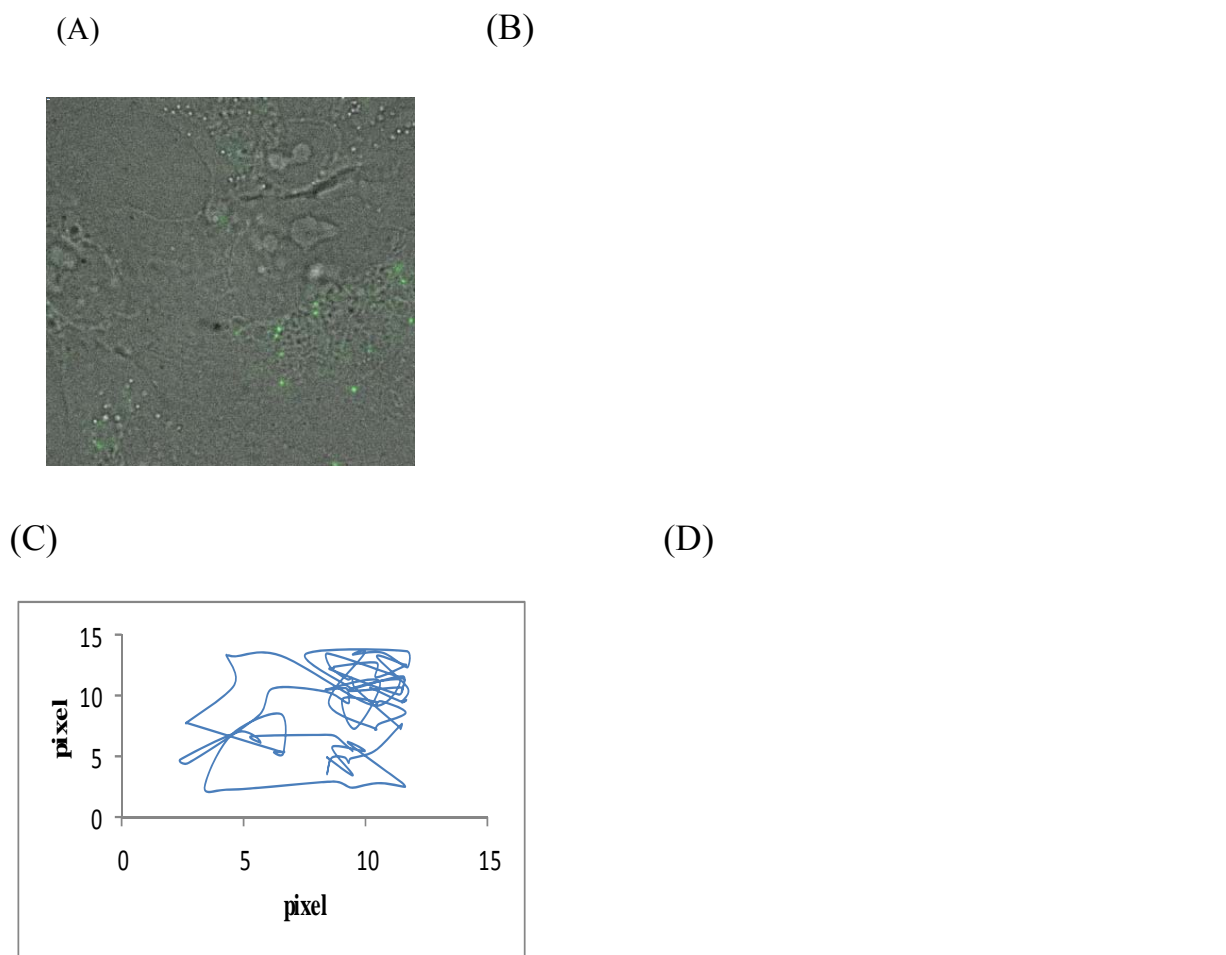


Figure S12. (A) Representative confocal microscope image, (B) photoluminescence intensity trajectory, (C) diffusion trajectory, and (D) the mean square displacement of green emitting  $\text{CdS}_{0.75}\text{Se}_{0.25}$  quantum dots coated with mercaptopropionic acids.