

EuS-CdS and EuS-ZnS Heterostructured Nanocrystals Constructed from Co-thermal Decomposition of Molecular Precursors in Solution Phase

Xueyun Gong,^[a,b,c] Zhengqing Liu,^[a] Dong Yan,^[a] Hongyang Zhao,^[a] Na Li,^[a] Xinyu Zhang,^[a] and Yaping Du^{*[a,b]}

Experimental Section

Chemicals

Europium nitrate hexahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, >99.99%, Sigma-Aldrich), 1,10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2$, >99%, Sigma-Aldrich), sodium diethyldithiocarbamate trihydrate ($\text{Na}(\text{ddtc}) \cdot 3\text{H}_2\text{O}$, >99%, Sigma-Aldrich), cadmium chloride hydrate ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$, >98%, Tianjin Zhiyuan Chemical Company), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, >98%, Tianjin Zhiyuan Chemical Company), oleic acid (OA, 90%, Alpha), oleylamine (OM, >80%, Acros), 1-octadecene (ODE, >90%, Acros), absolute ethanol ($\text{C}_2\text{H}_6\text{O}$, >99.7%), and cyclohexane (C_6H_{12} , >99.5%) were used as received without further purification.

Synthesis of $\text{Eu}(\text{ddtc})_3(\text{Phen})$

The precursor $\text{Eu}(\text{ddtc})_3(\text{Phen})$ was synthesized *via* a slightly modified method developed by Formanovskii et al.^[1] In a typical procedure, a solution of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5 mmol of it dissolved in 20 mL of distilled water) was added to the solution of 1,10-phenanthroline (5 mmol of it dissolved in 30 mL of boiling distilled water) under vigorous stirring. Then $\text{Na}(\text{ddtc}) \cdot 3\text{H}_2\text{O}$ solution (18 mmol of it dissolved in 40 mL of distilled water and filtered to obtain the filtrate) was added into the above mixture drop by drop. Immediately, the deep-orange-colored precipitate was produced and then the as-formed precipitate was filtered and dried in vacuum oven at 60 °C overnight for further use.

Synthesis of $\text{Cd}(\text{ddtc})_2$ and $\text{Zn}(\text{ddtc})_2$

In a typical procedure, drop by drop addition of $\text{Na}(\text{ddtc}) \cdot 3\text{H}_2\text{O}$ solution (12 mmol of it dissolved in 40 mL of distilled water and filtered to obtain the filtrate) to the $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (5 mmol of it dissolved in 20 mL of distilled water) under vigorous stirring, respectively. A white precipitate was immediately resulted and then the as-formed precipitate was filtered and dried in vacuum oven at 60 °C overnight for further use.

Synthesis of EuS-CdS heterostructured NCs

The EuS-CdS heterostructured NCs were prepared *via* co-thermal decomposition of molecular precursors of $\text{Cd}(\text{ddtc})_2$ and $\text{Eu}(\text{ddtc})_3(\text{Phen})$ in the mixed solvent of oleic acid, oleylamine and 1-octadecene. Typically, 0.3 mmol of $\text{Cd}(\text{ddtc})_2$ was placed in mixed solvent of oleic acid (3 mmol), oleylamine (18 mmol) and 1-octadecene (20 mmol) in a three-neck flask (100 mL) at room temperature. Subsequently, the mixture was heated to 120 °C and degassed for ~30 min, thus forming a

homogeneous solution. Then the temperature was rapidly increased to 280 °C under pure nitrogen atmosphere. The growth processes of CdS proceed at 280 °C for 10 min. Subsequently, a slurry of $\text{Eu}(\text{ddtc})_3(\text{Phen})$ (0.1 mmol) dispersed in 1.0 g (3.7 mmol) of oleylamine was swiftly injected into the above-mentioned solution. The reaction then sustained for ~20 min. After cooled down to room temperature, the products were separated by adding an excess amount of ethanol and collected from the solution by centrifugation (8500 rpm), followed by drying in an vacuum oven at 60 °C overnight for further characterizations. The as-dried NCs had a yield greater than 60 %, and could be easily re-dispersed in various non-polar organic solvents such as cyclohexane.

Synthesis of EuS-ZnS heterostructured NCs

The preparation of EuS-ZnS was similar to nanoheterostructures that of EuS-CdS, except that the growth of ZnS by thermal decomposition of $\text{Zn}(\text{ddtc})_2$ and then proceed at 280 °C for 5 min. The as-harvested NCs had a yield greater than 60 %, and could be easily re-dispersed in various non-polar organic solvents such as cyclohexane.

Characterization

The morphologies of the as-obtained products were observed by the transmission electron microscopy (TEM, Hitachi HT-7700, Japan) operating at 100 kV. The detailed structure and the chemical composition of the heterostructures were analyzed using high-resolution transmission electron microscopy (HRTEM, Tecnai G² F20 S-TWIN, USA) and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM, Tecnai G² F20 S-TWIN, USA) operated at 200 kV. The crystal phase of the samples was checked by power X-ray diffraction (XRD, Rigaku D/MAX-RB, Japan) with a scanning rate of 5 °/min from 10 ° to 80 °, using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Energy dispersive X-ray spectroscopy (EDAX) characterizations were performed on scanning electron microscopy (SEM, FEI Quanta F250, USA). X-ray photoelectron spectroscopy (XPS) data were obtained using a Escalab 250 xi photoelectron spectrometer using Al K radiation (15 kV, 225 W, base pressure~ 5×10^{-10} Torr). The Fourier transform infrared absorption (FTIR) spectra were carried on NICOLET 6700 FT-IR (USA). Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 Spectro Fluorophotometer (Japan) at room temperature. Thermal analysis was performed on a Setaram evolution 2400 (France), the data were collected from 30 °C to 600 °C under nitrogen gas flow of 20 mL/min, and heating rate was set at 10 °C/min. Magnetic measurements were performed using a Superconducting Quantum Interference Device (SQUID) XL-7 magnetometer (Quantum Design, USA).

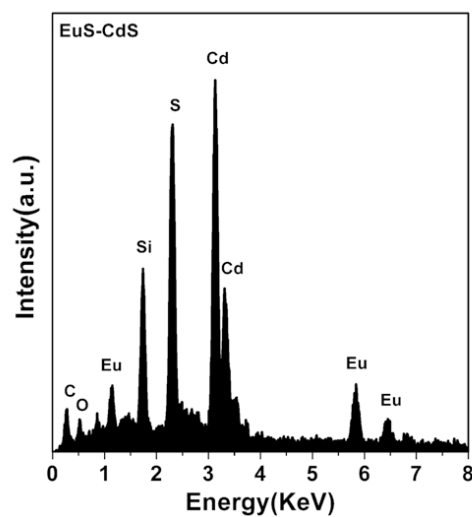


Figure S1 EDAX spectrum of EuS-CdS heterostructured NCs.

Table S1 The element ratio in EuS-CdS compound estimated from the EDAX spectrum

Elements	Weight %	Atomic %
C	12.38	42.74
O	5.08	6.52
Si	7.18	10.6
S	15.35	19.85
Cd	40.87	15.07
Eu	19.14	5.22

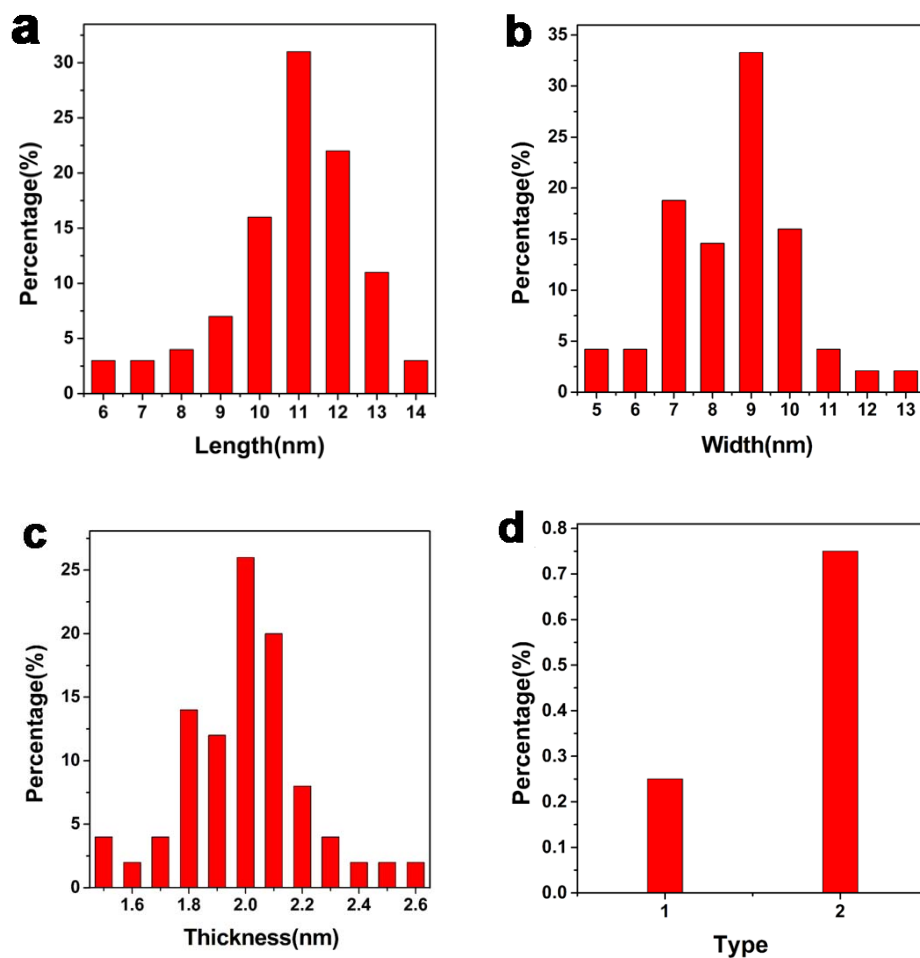


Figure S2 The CdS (a) length and (b) width distribution in EuS-CdS heterostructured NCs; (c) The EuS thickness distribution in EuS-CdS heterostructured NCs; (d) The morphology distribution of EuS-CdS heterostructured NCs, type 1 represents the EuS grew on one side of CdS, type 2 represents the EuS grew on both two sides of CdS.

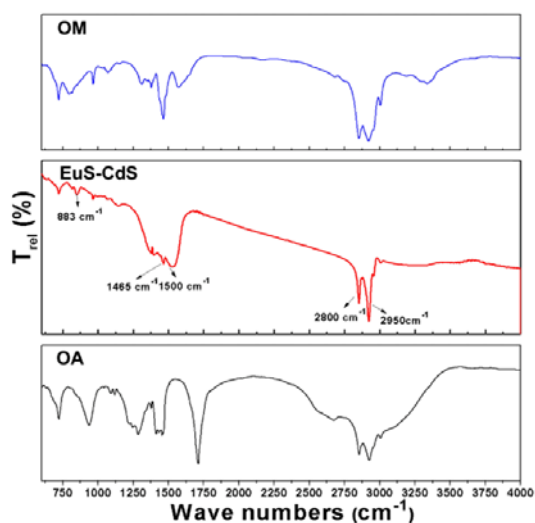
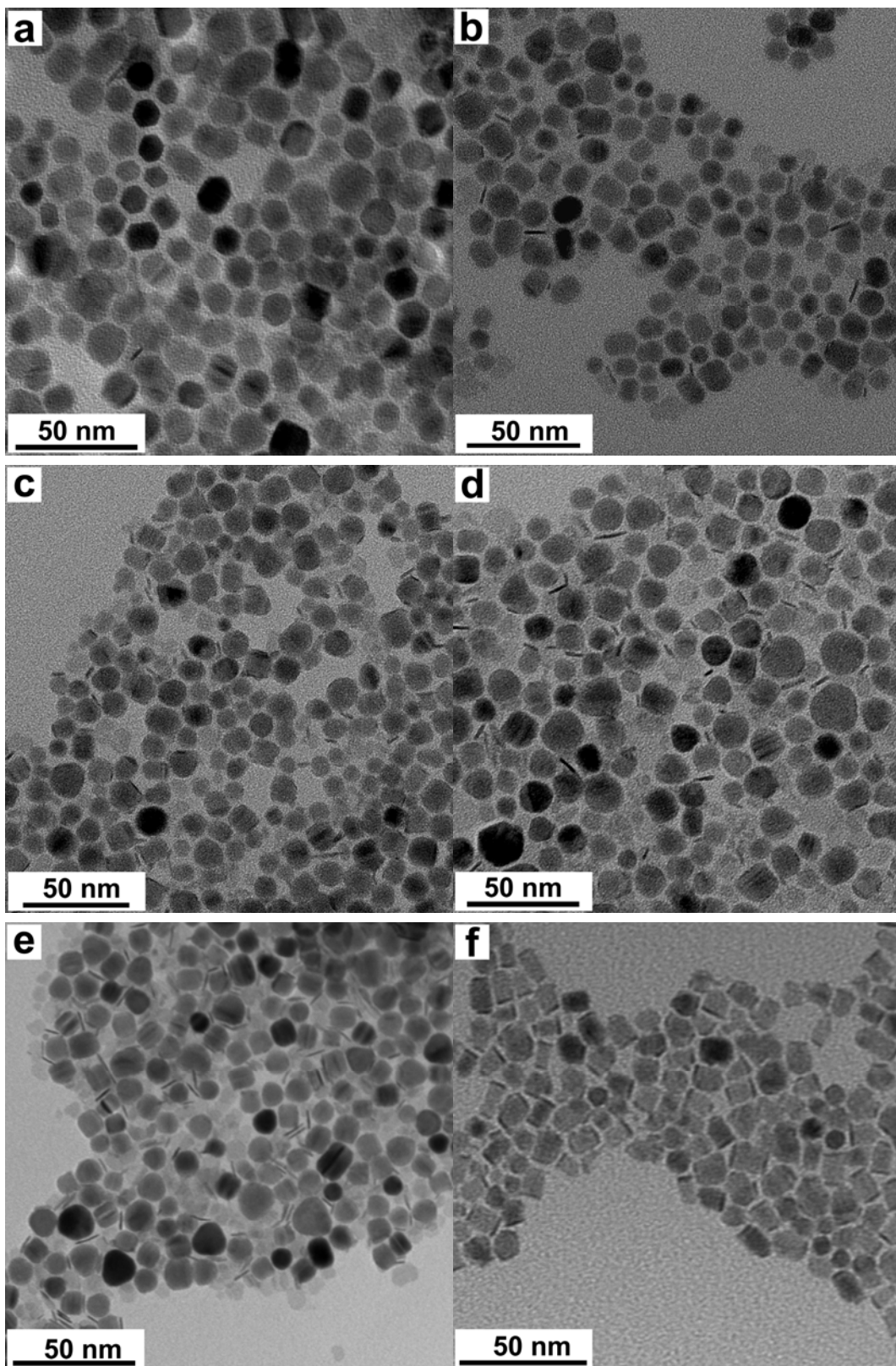


Figure S3 The FTIR spectra of EuS-CdS heterostructured NCs.



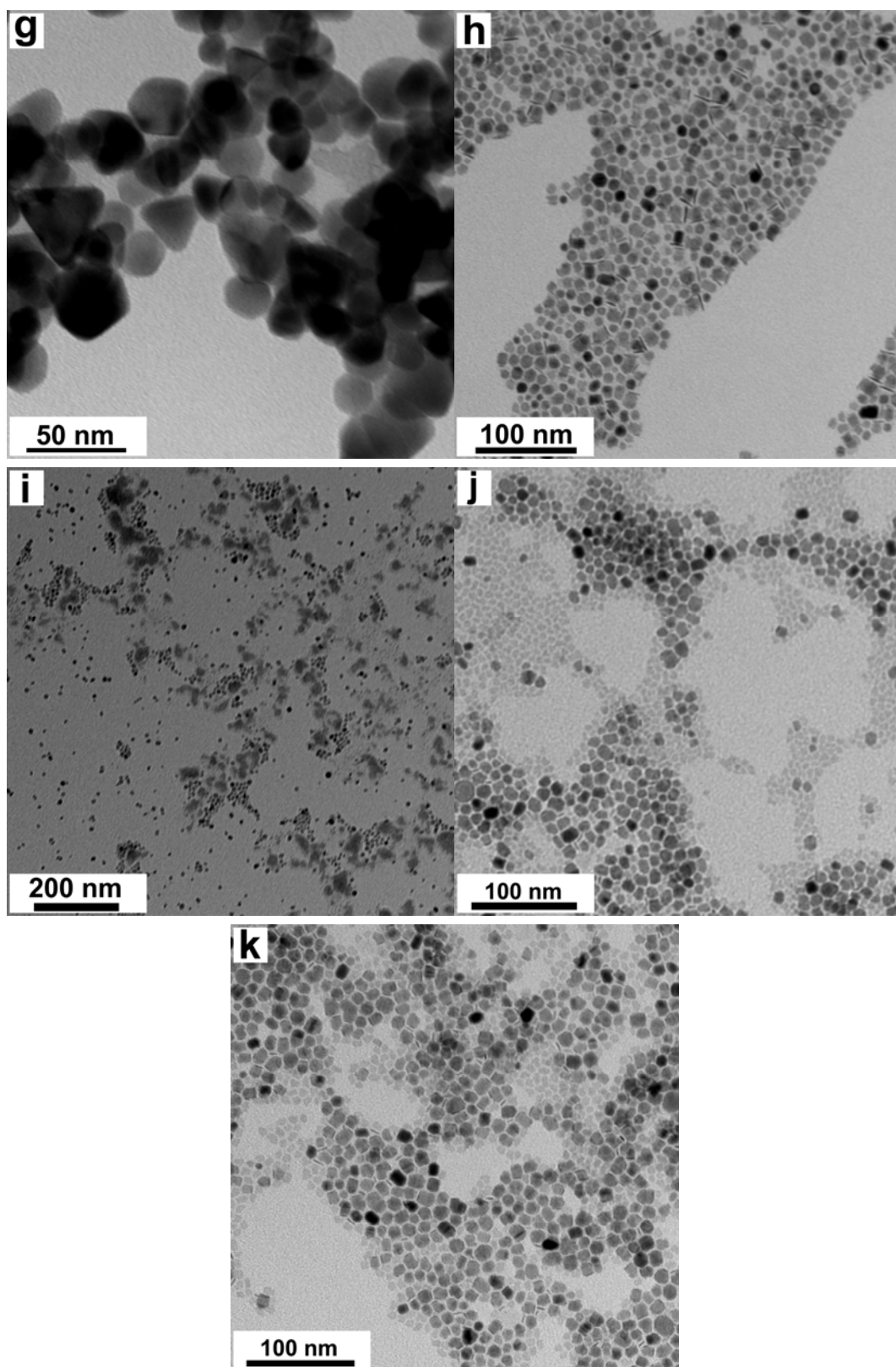


Figure S4 TEM images of EuS-CdS products with different mole ratio of $\text{Cd}(\text{ddtc})_2$ and $\text{Eu}(\text{ddtc})_3(\text{Phen})$: (a) 9:1, (b) 7:1, (c) 5:1, (d) 4:1, (e) 1:1 and (f) 3:1. TEM images of EuS-CdS products with different mole ratio of oleic acid and oleylamine: (g) 3:1 and (h) 1:9. TEM image of products with different reaction temperature: (i) 250 °C, (j) 260 °C and (k) 270 °C.

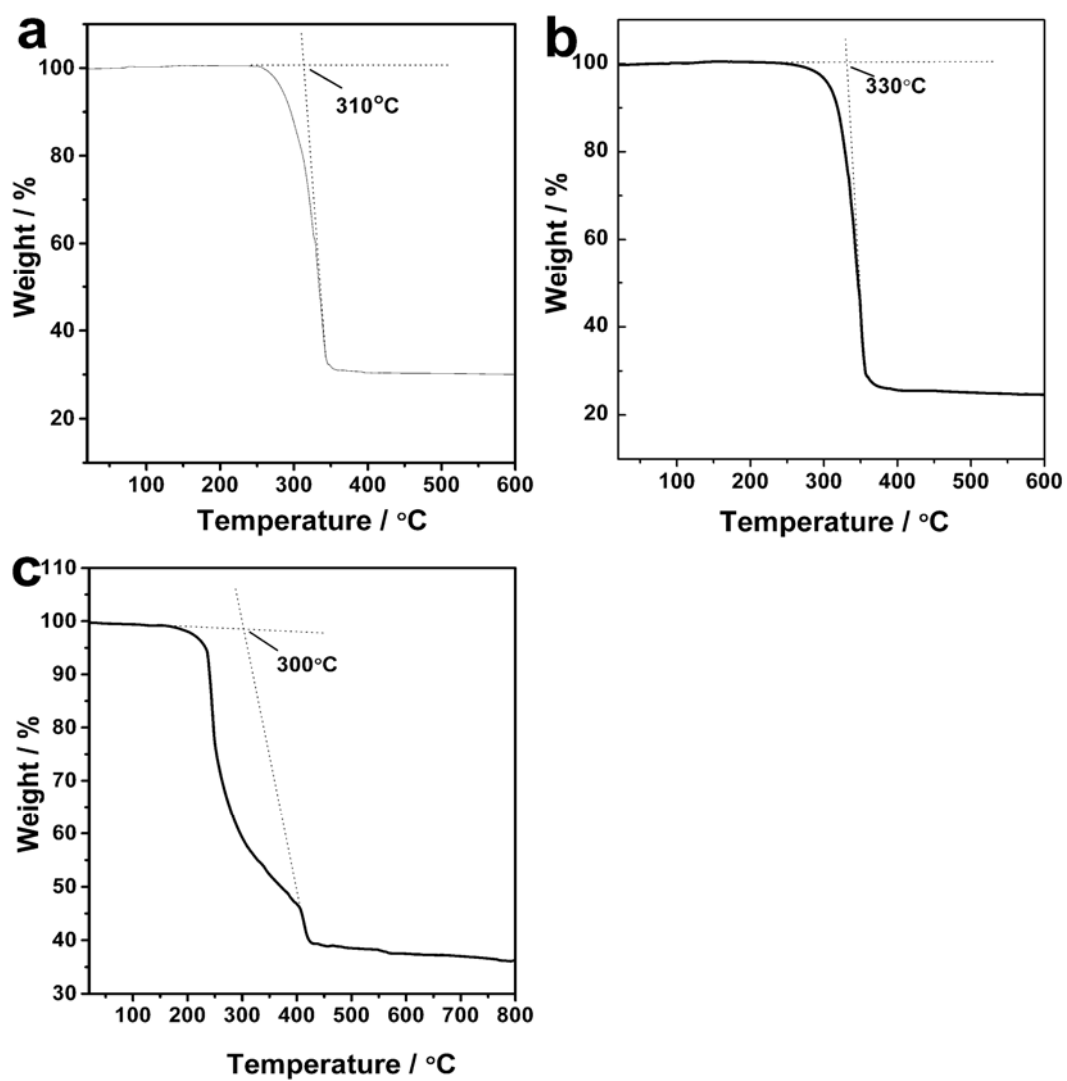


Figure S5 Thermogravimetric analysis of molecular precursors of (a) $\text{Cd}(\text{ddtc})_2$, (b) $\text{Zn}(\text{ddtc})_2$ and (c) $\text{Eu}(\text{ddtc})_3(\text{Phen})$.

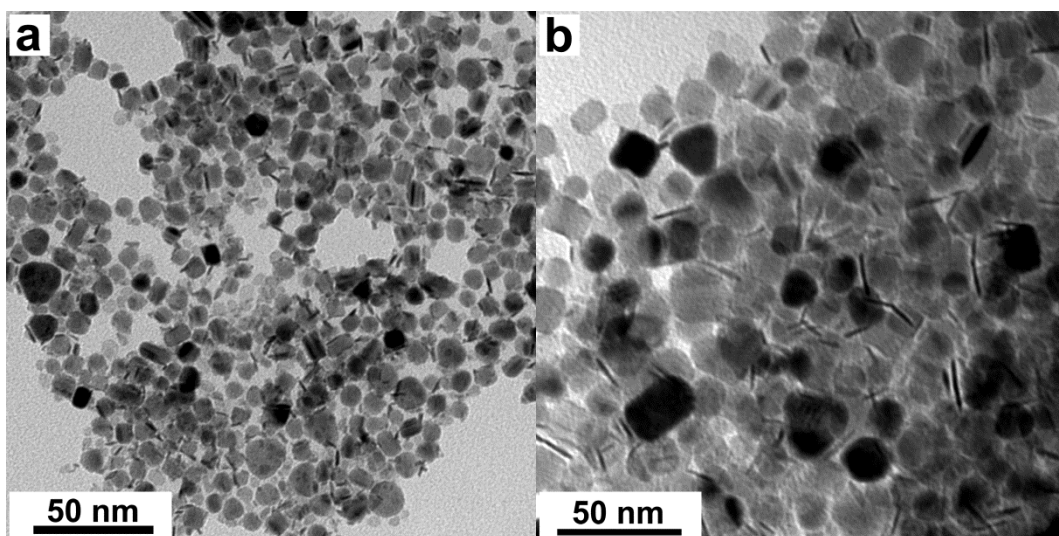


Figure S6 (a) TEM image of EuS-CdS products with the reaction temperature was 300 °C; (b) TEM image of EuS-CdS products with the reaction time was 1 h.

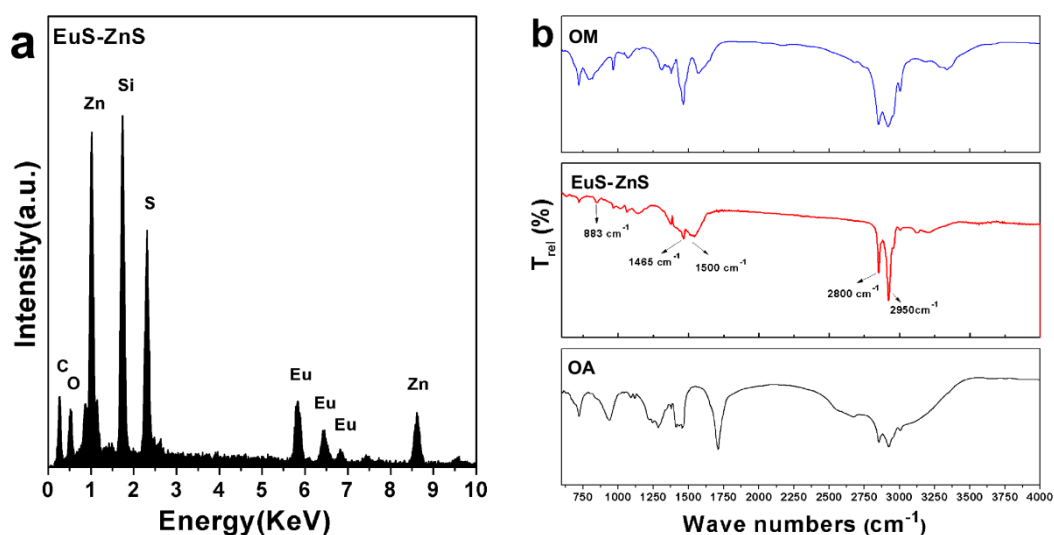


Figure S7 (a) EDAX and (b) FTIR spectra of EuS-ZnS heterostructured NCs.

Table S2 The element ratio in EuS-ZnS compound estimated from the EDAX spectrum

Element	Weight %	Atomic %
C	29.96	58.34
O	9.08	13.28
Si	14.16	11.79
S	10.41	7.6
Eu	19.77	3.04
Zn	16.63	5.95

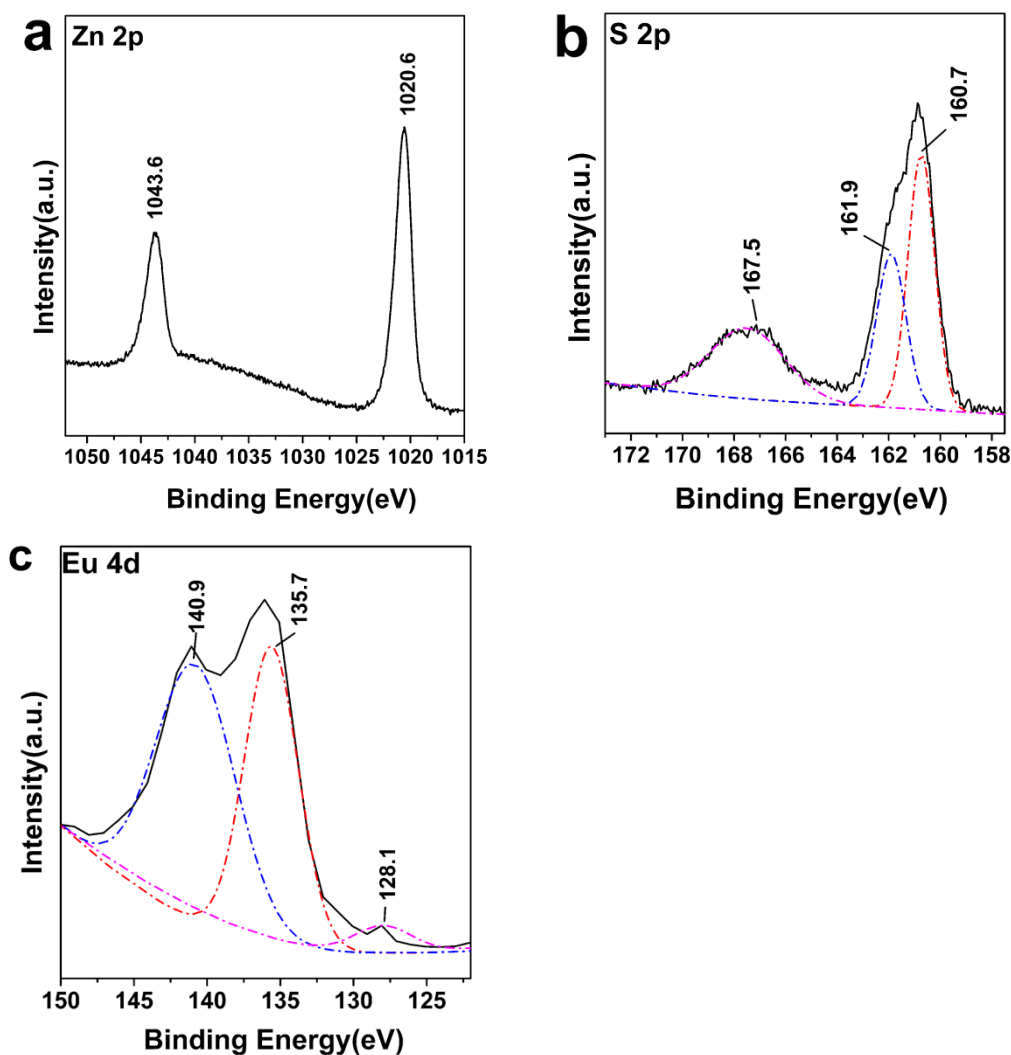


Figure S8 XPS spectra of (a) Zn 2p, (b) S 2p, (c) Eu 4d signals recorded for EuS-ZnS heterostructured NCs. As seen from Fig. S6(a), the double peaks at 1043.6 and 1020.6 eV are assigned to the Zn 2p_{1/2} and Zn 2p_{3/2} levels of Zn²⁺ ions, respectively. The peaks shown in Fig. S6(b) located at 162.6 and 161.4 eV could be assigned to the binding energies of S 2p_{1/2} and S 2p_{3/2}, respectively. The peaks shown in Fig. S6(c) located at 140.9 and 135.7 eV are assigned to the Eu 4d_{3/2} and Eu 4d_{5/2} levels of Eu³⁺ ions, while the peaks at 128.1 eV was assigned to the Eu 4d levels of Eu²⁺ ions, indicating that the Eu²⁺ ions on the surface could be partly oxidized to Eu³⁺ ions while exposing in air.

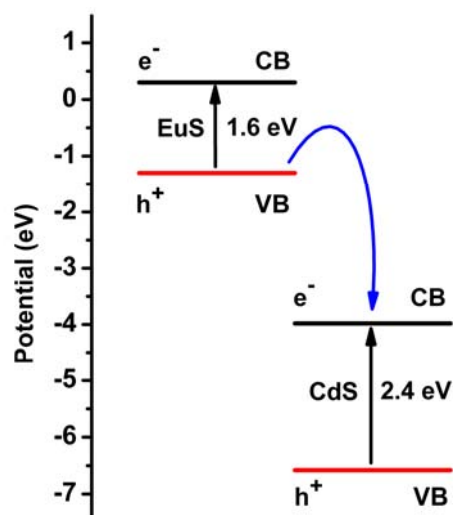


Figure S9 The energy band structure scheme of EuS-CdS heterostructured NCs.

Reference:

- [1] R. A. Ivanov, I. E. Korsakov, A. A. Formanovskii, S. E. Paramonov, N. P. Kuz'mina and A. R. Kaul, *Russ. J. Coord. Chem.* 2002, **28**, 670–672.