Supporting Information

Experimental and Theoretical Studies on the Controlled Synthesis of Alkali-Metal-Doped Rare-Earth Oxysulfide Nanocrystals

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Experimental Sections

**Chemicals:** Oleic acid (OA, 90%; Aldrich), oleylamine (OM, >80%; Acros), 1-octadecylamine (ODA, >90%; Acros), RE$_2$O$_3$ (RE = La, Eu, Gd, Tb, Yb and Lu, >99%; Beijing Founder & Dong-An Rare Earth Advanced Materials Co. Ltd., China), sulfur (S, A.R.; Beijing Yili Fine Chemical Co. Ltd., China), lithium acetylacetonate (Li(acac), 97%; Sigma), potassium hydroxide (KOH, >96%; Beijing Chemical Works, China), acetylacetone (Hacac, A.R.; Beijing Yili Fine Chemical Co. Ltd., China), ammonia (NH$_3$·H$_2$O, AR; Beijing Chemical Works, China), methanol (CH$_3$OH, A.R.; Beijing Chemical Works, China), absolute ethanol (C$_2$H$_5$OH, AR; Beijing Chemical Works, China), cyclohexane (C$_6$H$_{12}$, AR; Beijing Chemical Works, China).

**Synthesis of RE(acac)$_3$ precursors:** Rare-earth acetylacetonate (RE(acac)$_3$, RE = La, Eu, Gd, Tb, Yb and Lu) was prepared by following the synthetic procedure described in Ref. S1.

**Synthesis of K(acac) precursor:** Potassium acetylacetonate (K(acac)) was prepared by following the synthetic procedure described in Ref. S2.

**Synthesis of alkali metal doped RE$_2$O$_2$S nanocrystals:** In a typical synthesis route, La(acac)$_3$ (0.5 mmol), K(acac) (0.5 mmol), S (1.0 mmol), OA (2.5 mmol), OM (17 mmol), and ODE (20 mmol) were added in a three-neck flask (100 mL) at RT. The mixture was heated to 120°C under vacuum for 30 min to remove water and other impurities with low boiling points. Then the temperature was raised to 310°C at a rate of 20°C/min under a high purified N$_2$ atmosphere. In this process, the solution turned to transparent at 240°C. The system was cooled to RT after 30 min reaction. La$_2$O$_2$S nanocrystals were precipitated by absolute ethanol after dispersed by cyclohexane and centrifuging at 7800 r/min.

Other K doped RE$_2$O$_2$S nanocrystals (RE = Eu, Gd, and Yb) and Li doped La$_2$O$_2$S nanocrystals were prepared with the same procedure by changing the species of precursors.

Eu, K or Tb, K co-doped nanocrystals were also synthesized with the procedure above, and Eu(acac)$_3$ or Tb(acac)$_3$ was added as precursors respectively. The doping proportions of Eu and Tb were 4% and 1%, respectively, which were the same as those of normal commercial fluorescent powders.
**Instrumentation**

**XRD:** The powder XRD patterns were characterized on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of 1/2° at a 20 scanning speed of 8° min⁻¹ under Cu Kα radiation (λ =1.5406 Å).

**TEM, HRTEM, EDS & SAED:** Samples for transmission electron microscopy (TEM) analysis were prepared by drying a drop of diluted colloid solution of doped RE₂O₅ nanocrystals in cyclohexane on copper grids coated by amorphous carbon. High resolution TEM (HRTEM), energy dispersive X-ray spectroscopy (EDS), and Selected Area Electron Diffraction (SAED) analyses were performed on a FEG-TEM (JEM-2100F, JEOL, Japan) operated at 200 kV.

**Photoluminescence:** The UV-simulated photoluminescence properties of Eu, K and Tb, K co-doped La₂O₅ nanocrystals were measured at RT on a Hitachi F-4500 fluorescence spectrophotometer (Japan) with a Xenon lamp as a stimulation source. The scanning speed was fixed at 60 nm-min⁻¹ with both the excitation and emission splits fixed at 2.5 nm. The lifetime measurements of the nanoplates were obtained on an Edinburgh Instruments FLS920 transient/steady-state fluorescence spectrometer at room temperature. The PL quantum yields of the nanocrystals were measured by the absolute method using integrating sphere of Horiba Jobin Yvon Nanolog system. The coordinations in the xy-chromaticity diagram are directly calculated from the fluorescent spectra (CIE 1931).
Supplementary Data

**Figure S1.** TEM image and EDS results of Lu$_2$O$_3$:K nanocrystals.
Density Functional Calculations of alkali metal doped RE$_2$O$_2$S

Figure S2. Phase diagrams of undoped RE$_2$O$_2$S, and alkali metal doped La$_2$O$_2$S.
Figure S3. EDS results of Eu$_2$O$_2$S:K, Gd$_2$O$_2$S:K and Yb$_2$O$_2$S:K nanocrystals.
Figure S4. EDS results of (a) Eu, K and (b) Tb, K co-doped La$_2$O$_2$S nanocrystals. The doping proportions of Eu and Tb were determined as 4% and 1%, respectively.
Figure S5. XRD patterns of K-doped La$_2$O$_2$S:Eu ($a = 4.044$ Å, $c/a = 1.854$, $V = 106.2$ Å$^3$) and La$_2$O$_2$S:Tb NCs ($a = 4.039$ Å, $c/a = 1.776$, $V = 101.3$ Å$^3$). The standard XRD pattern of La$_2$O$_2$S (JCPDS 27-0263) is also shown in the panel for a reference.
**Figure S6.** Luminescence decay curves (exponent coordinates is used for intensity axis) of the 622 nm emission of Eu$^{3+}$ ions in Eu, K co-doped La$_2$O$_2$S nanoplates. Inset is a digital photo of the Eu, K co-doped La$_2$O$_2$S nanoplates showing strong red emission under UV light excitations.
Figure S7. (a) Room temperature excitation spectra of Tb,K co-doped nanoplates with emission of 542 nm. The excitation band at 262 nm is ascribed to the $4f^8$ to $4f^75d^1$ transition of Tb$^{3+}$ (Ref. 3a). (b) Luminescence decay curves (exponent coordinates is used for intensity axis) of the 542 nm emission of Tb$^{3+}$ ions in Tb, K co-doped La$_2$O$_2$S nanoplates.
Figure S8. Fluorescence emission spectrum of Tb,K co-doped La$_2$O$_2$S nanocrystals under 262 nm UV excitation. The widths of emission and excitation slits are both 2.5 nm.