Electronic Supplementary Information (ESI)

3D-hierarchical Lu$_2$O$_2$S:Eu$^{3+}$ micro/nano-structures: controlled synthesis and luminescence behavior

Qi Zhao,$^{ab}$ Yuhua Zheng,$^{ab}$ Ning Guo,$^{ab}$ Yongchao Jia,$^{ab}$ Hui Qiao,$^{ab}$ Wenzhen Lv$^{ab}$ and Hongpeng You$^{*a}$

$^a$State key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China.

$^b$Graduate University of the Chinese Academy of Sciences, Beijing 100049, P. R. China.

*Corresponding author: E-mail address: hpyou@ciac.jl.cn

Figure S1  XRD patterns of lutetium oxysulfide precursors prepared at pH values of 4 (a) and 8 (b).

Figure S2  FT-IR spectra of lutetium oxysulfide precursors prepared at pH values of 4 (a) and 8 (b).
According to EDS result (Figure S2), no elements other than O, S, C, and Lu are present except the Au peaks from measurement. Infrared spectra (Figure 2) show that stretching modes such as $\nu_{\text{OH}}$ (3400–3600 cm$^{-1}$), $\nu_{\text{CH}}$ (2945 cm$^{-1}$), $\nu_{\text{C=O}}$ (1650–1670 cm$^{-1}$), $\nu_{\text{C=N}}$ (1520–1540 cm$^{-1}$), $\nu_{\text{C=S}}$ (1080–1140 cm$^{-1}$) and deformation modes such as $\delta_{\text{Lu-S}}$ (605 cm$^{-1}$) and $\delta_{\text{Lu-O}}$ (570–580 cm$^{-1}$) are clearly visible.$^{1,2}$ Taking the sample at pH = 4 (Figure S3) as an instance, the broad absorption band located around 3504 cm$^{-1}$ is assigned to O–H groups from the adsorbed ethylene glycol and ethanol. The peak located at 1660 cm$^{-1}$ is attributed to the C=O stretching, which red-shifts compared to that of pure 10 PVP, indicating that the PVP is coordinated with lanthanide ions on the surface of the precursors.$^{3,4}$ The blue shift of the C-N stretching vibration from 1474 cm$^{-1}$ in pure thiourea to 1534 cm$^{-1}$ implies that the sulfur atom is bonding with the metal ion in the precursor. The C=S stretching vibration at 1084 cm$^{-1}$ in pure thiourea is split into two peaks of 1080 and 1134 cm$^{-1}$ because of the formation of a metal-sulfur bond.$^{5,6}$ An analogous result has been obtained in sample at pH = 8. On the basis of the above analysis, the lutetium oxysulfide precursor can be presumed as an inorganic-organic complex compound which constitutes Lu–O, Lu–S, O–H, –CH$_2$– and C–N bonds.
Table S1  The atomic ratios of Lu and Eu in the samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Atomic ratios of Lu and Eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>straw-sheaf</td>
<td>94.09:5.90</td>
</tr>
<tr>
<td>spherulite</td>
<td>93.91:6.08</td>
</tr>
<tr>
<td>microflower</td>
<td>94.06:5.94</td>
</tr>
</tbody>
</table>

In spite of tiny difference, the three samples can be considered to have same concentration of europium ions. Although the concentrations of europium ions deviate from the expected 5%, it is still feasible to compare the PL intensity provided that the concentrations of Eu$^{3+}$ are identical in the samples.

References