

Supporting Information

Self-assembly and multicolor emission of core/shell structured CaWO₄:Na⁺/Ln³⁺ spheres

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Table S1 Initial molar ratios and those measured by ICP technique for the as-prepared samples CaWO₄:Na⁺/Ln³⁺

Ln ³⁺	Initial molar ratios Ca:Ln:W	ICP results* Na:Ca:Ln:W	Formula
Dy ³⁺	0.925 : 0.075 : 1	0.128 : 0.858 : 0.071 : 1	Ca _{0.858} (Dy,Na) _{0.142} WO ₄
Tb ³⁺	0.85 : 0.15 : 1	0.131 : 0.744 : 0.128 : 1	Ca _{0.744} (Tb,Na) _{0.256} WO ₄
Sm ³⁺	0.925 : 0.075 : 1	0.165 : 0.884 : 0.058 : 1	Ca _{0.884} (Sm,Na) _{0.116} WO ₄
Eu ³⁺	0.925 : 0.075 : 1	0.121 : 0.868 : 0.066 : 1	Ca _{0.868} (Eu,Na) _{0.132} WO ₄

* In the as-prepared samples, the concentration of Na⁺ ions is larger than Ln³⁺ (Ln=Dy, Tb, Sm, Eu). The presence of excess sodium in all samples may be the consequence of the co-doping of Ln³⁺ and Na⁺ at Ca²⁺ sites and the excess surface adsorption of Na⁺.

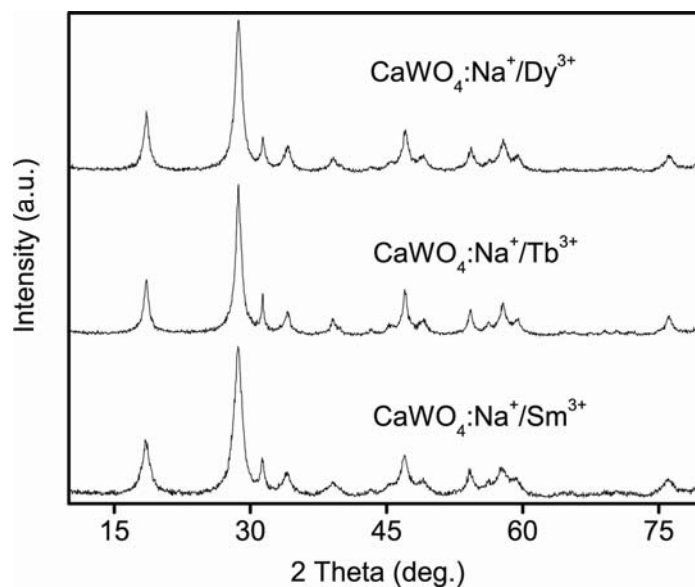


Fig. S2 XRD patterns of $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$ spheres ($\text{Ln} = \text{Dy}, \text{Tb}, \text{Sm}$). These XRD data matched well that for $\text{Ln}=\text{Eu}$. Using the Scherrer formula for (101) diffraction peak, the mean sizes for $\text{Ln} = \text{Dy}, \text{Tb}$, and Sm were calculated to be 11.5, 11.7, and 7.7 nm, respectively.

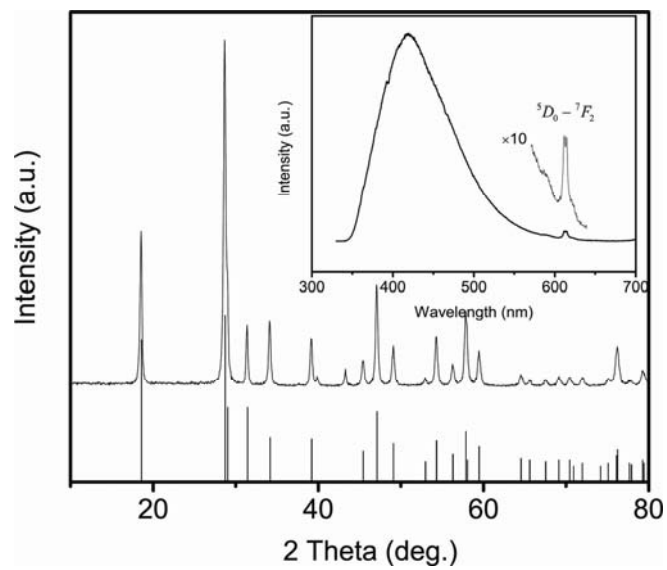


Fig. S3 XRD pattern of $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$ prepared in the citric acid free system. Inset is the corresponding emission spectrum.

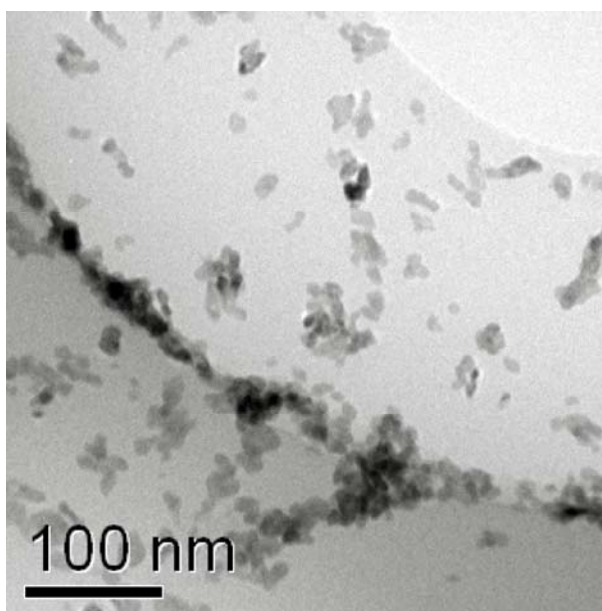


Fig. S4 TEM image of CaWO_4 nanocrystals prepared in the PVP free system. The as-prepared CaWO_4 consists of nearly dispersed nanoparticles with a spindly shape. The diameter of spindly particle was about 16 nm.

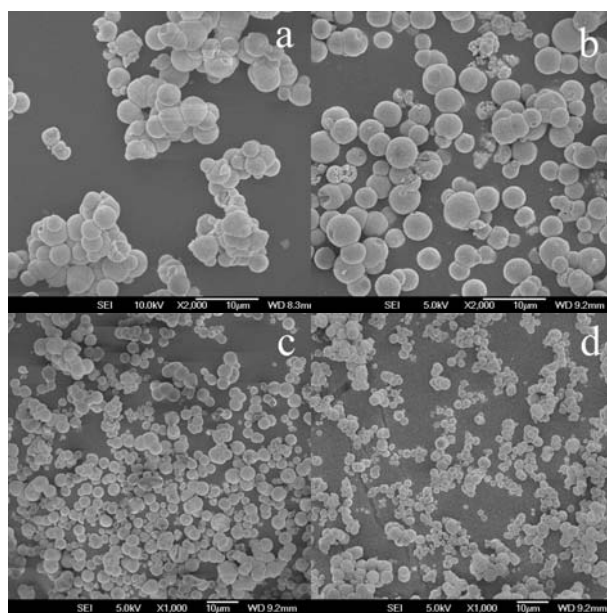


Fig. S5 SEM images of CaWO₄ spheres prepared with different PVP contents of (a) 0.3g, (b) 1.2g, (c) 1.8g, and (d) 2.4g.

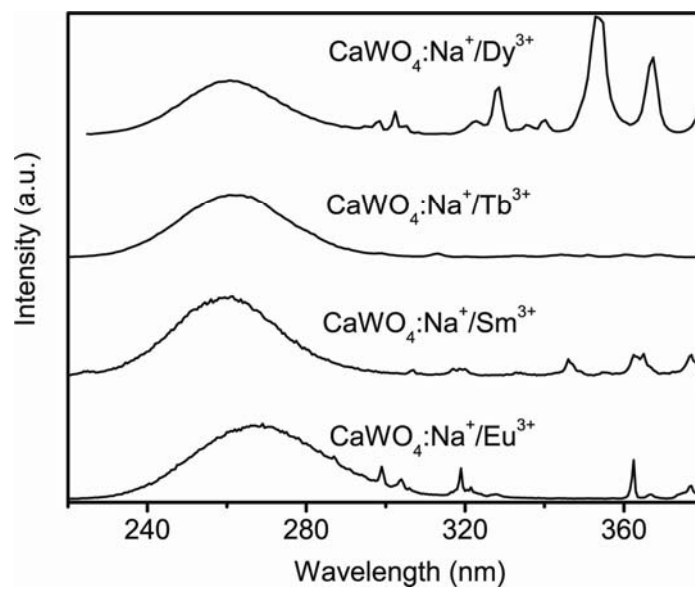


Fig. S6 Excitation spectra of the as-prepared CaWO₄:Na⁺/Ln³⁺ spheres (Ln=Dy, Tb, Sm, Eu).

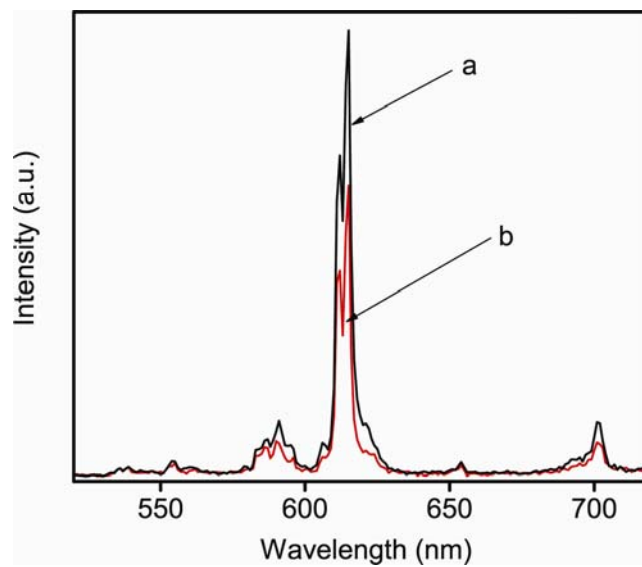


Fig. S7 Emission spectra of (a) $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$ spheres and (b) $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$ nanocrystals prepared in the absence of PVP.