Supplementary information

Chemical modifications of red phosphor $LaPO_4$:Eu^{3+} nanorods to generate white light

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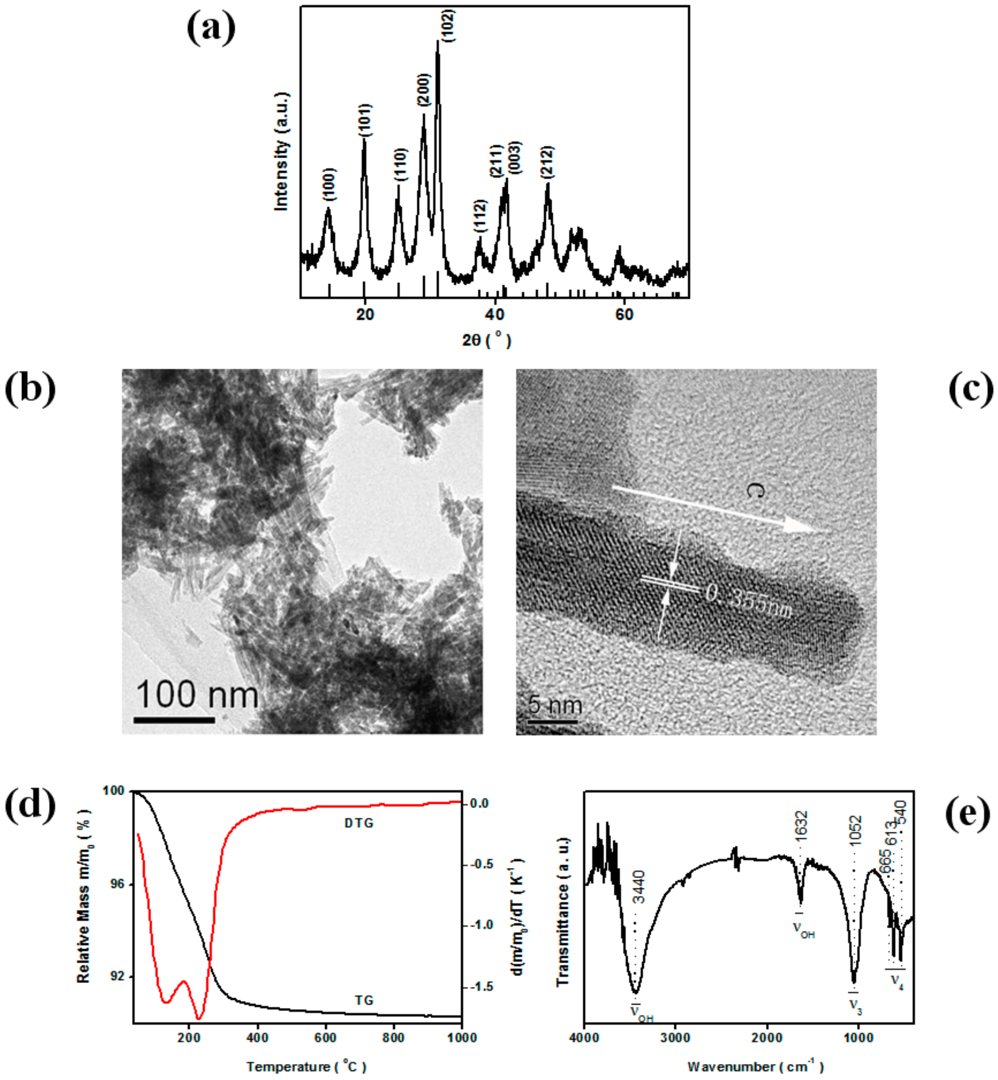
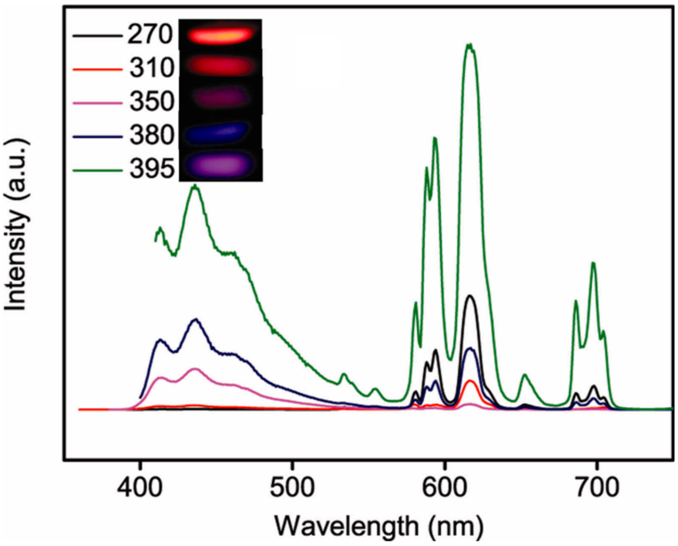
1. Chemical analysis using XRD, TEM, TG, and IR.

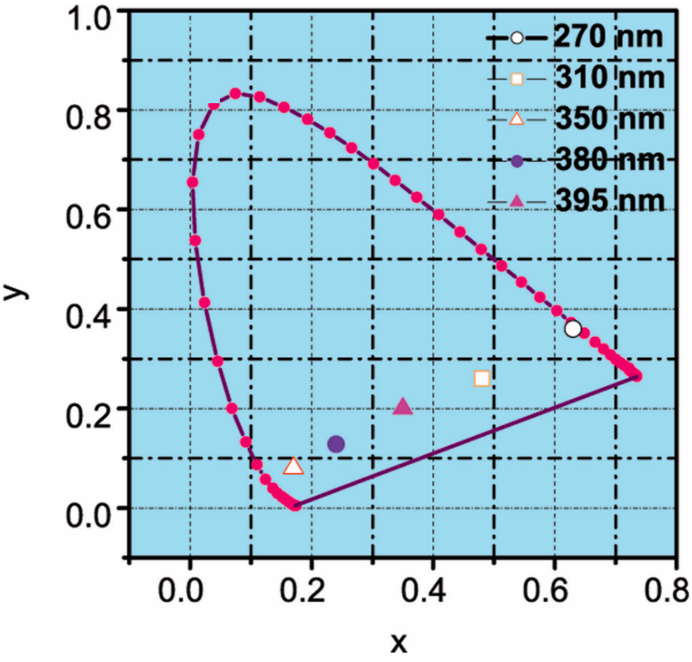


S1. Formation of $LaPO_4$:Eu^{3+} nanorods terminated with highly hydrated layers: (a) XRD, (b) TEM, (c) HRTEM images, (d) TG data, and (e) Infrared spectrum of the $LaPO_4$:Eu^{3+} nanorods without OA capping. Vertical bars of (a) denote the standard diffraction data of $LaPO_4 \cdot xH_2O$. Based on the half height width of peak (100), the crystallite size was calculated using Scherrer formula to be approximately 5.2 nm. From TEM, the sample is seen primarily composed of tiny rods with an axis ratio less than 10. All nanorods were fully crystallized into tiny crystals with rough surfaces, and the interplanar spacing was about 0.355 nm. Two step weight losses in its TG curve were observed. The first one occurred below 200 °C is associated with the release of 4-5% of residual water absorbed on the sample surface. The second one, beginning at about 200 °C and ending at about 400 °C, corresponds to the dehydration of the hydrated hexagonal $LaPO_4 \cdot xH_2O$ phase (rhabdophane-type). The total weight loss for the second step which corresponded to a hydration ratio x of the compound was estimated about 0.5. In the IR spectrum, only the modes of O-P-O, asymmetric bending vibration (ν_4), P-O asymmetric stretching vibration (ν_3), and O-H vibration from surface hydration were observed. These results indicated the highly hydrated terminations of the $LaPO_4:Eu^{3+}$ nanorods.

2. Photoluminescence

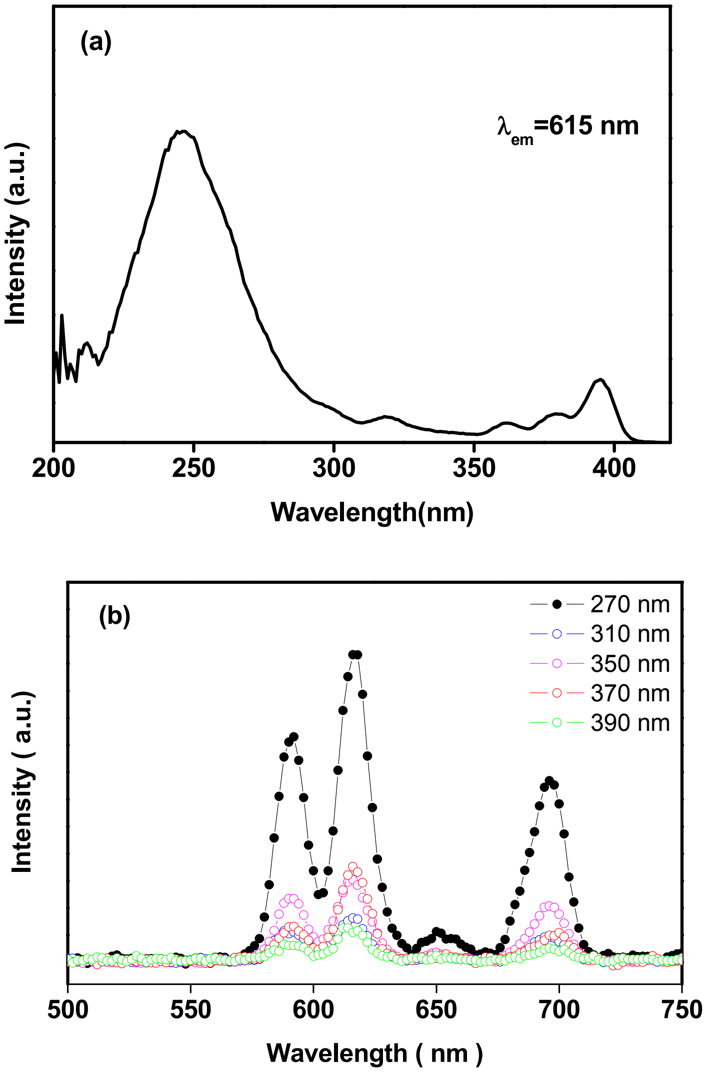


(a)



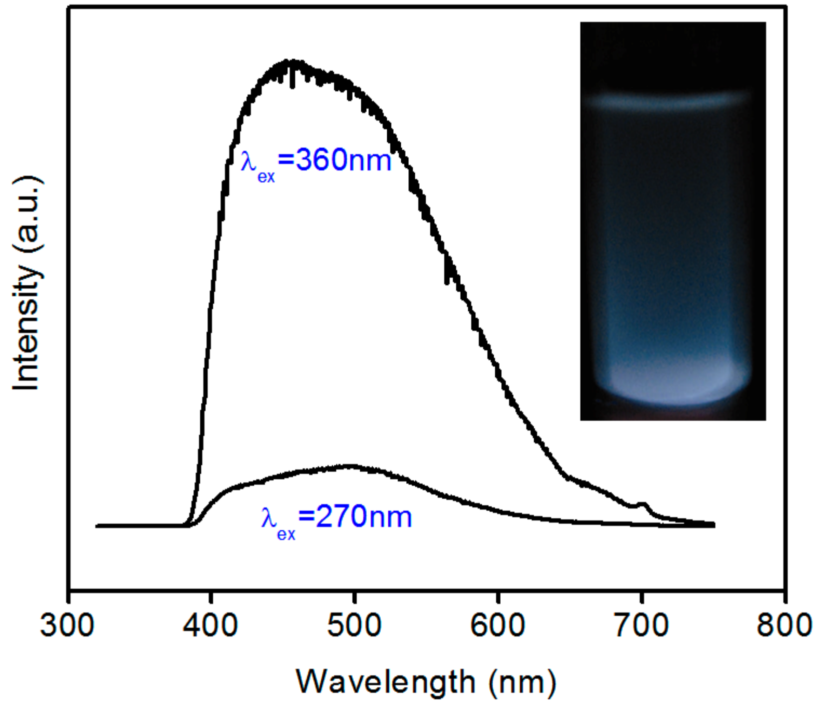
(b)

S2. (a) Photoluminescence and (b) CIE chromaticity diagram of the bulk monoclinic $LaPO_4:Eu^{3+}$ when excited at different wavelength monitored at 617 nm. Inset shows direct view photographs of tunable color emission from red to blue when excited at given wavelength. Bulk monoclinic $LaPO_4:Eu^{3+}$ was prepared by solid state reactions. Starting chemicals of La_2O_3, Eu_2O_3, and $NH_4H_2PO_4$ were first mixed and calcined in air at 900 °C for 3 hours. The obtained product was added into 50 mL aqueous solution containing 1 mL oleic acid and stirred vigorously for 2 hours. Finally, the product was washed with ethanol for several times.

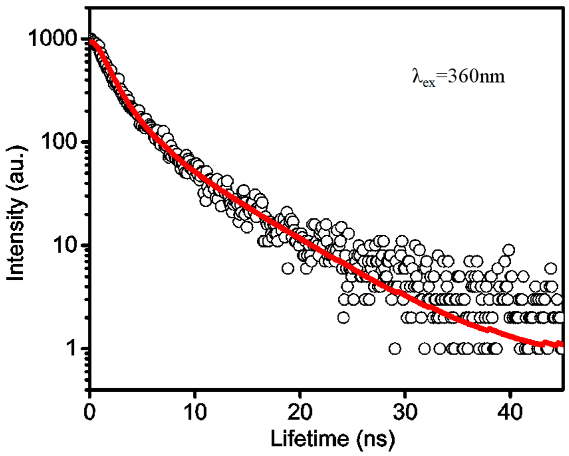


S3. (a) Excitation spectrum of the $LaPO_4:Eu^{3+}$ nanorods with no OA capping which was recorded with wavelengths monitored at λ_{em}= 615 nm, and (b) emission spectra of the $LaPO_4:Eu^{3+}$ nanorods with no OA capping which were excited at given wavelength. For the excitation spectrum, one broad band centered at 250 nm and several weak lines in the range of 400-450 nm were observed. The broad band is attributed to the Eu–O charge transfer, while the weak lines correspond to the direct excitation of the Eu^{3+} ground state to higher levels of the 4f-manifold [H. Meyssamy, K.

Riwotzki, A. Kornowski, S. Naused, M. Hasse, Adv. Mater. 11 (1999) 840]. For the emission spectra, when excited at 270 nm, four sharp emission lines located at 592, 615, 651, and 698 nm were observed, which are characteristic of the Eu^{3+} transitions from $^5D_0$ to ^7F_J (J=1, 2, 3, 4), respectively. The Eu^{3+} emissions were weakened obviously when excited at 310, 370, and 390 nm.



S4. Photoluminescence of OA-capped $LaPO_4$ nanorods when excited at 270 and 360 nm. Inset presents a direct view photograph of the nanorods dispersed in cyclohexane when excited at 360 nm.



S5. Luminescent decay of the OA-capped $LaPO_4:Eu^{3+}$ nanorods detected at 480 nm. The raw data were fitted into a double-exponential function, $I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$, where τ_1 and τ_2 are the fast and slow components of the luminescent lifetime, while A_1 and A_2 are the fitting parameters, respectively. The average lifetime is determined to be 5.38 ns, using the formula[1],

of $$\tau_{\mathrm{eff}} = \frac{\int_0^\infty tI(t)dt}{\int_0^\infty I(t)dt} = 16763/3118 \text{ ns.}$$

[1] Shionoya, S.; Yen, W. M. *Phosphor Handbook*; CRC Press: Boca Raton, FL, 1999.

S6. Relative intensities of $^5D_0$-$^7F_2$ transition of Eu^{3+} emission at 615 nm for given samples excited at various wavelength

λ_{ex} / nm	Relative Intensity		
	OA-capped $LaPO_4:Eu^{3+}$	$LaPO_4:Eu^{3+}$	bulk M-$LaPO_4:Eu^{3+}$
270	1	1	1
310	0.47	0.30	0.25
330	0.41	---	0.09
350	0.42	0.10	0.05
370	---	0.14	---
380	0.65	---	0.54
390	---	0.27	---
395	1.82	---	3.16

The relative intensity ratio of $^5D_0$-$^7F_2$ transition of Eu^{3+} emission at 615 nm under various excitations were obtained by taking the intensity under λ_{ex}=270 nm as unity, in which the raw emission data of three samples were adopted from Figures 7, S3, and S2, respectively. Distinct from other two samples, OA-capped $LaPO_4:Eu^{3+}$ sample showed emissions that are coupled with an apparent background. Therefore, the relative intensity ratio for OA-capped $LaPO_4:Eu^{3+}$ was calculated by subtracting the background contributed from the broad green-blue emission. It can be seen that under λ_{ex} =310 and 350 nm (i.e., not the characteristic excitations of Eu^{3+}), the relative intensity of $^5D_0$-$^7F_2$ transition of Eu^{3+} emission at 615 nm was significantly weakened for three samples. On the other hand, under λ_{ex} =350 nm, the relative intensity for OA-capped $LaPO_4:Eu^{3+}$ is 0.42, which is much higher than that of 0.10 for $LaPO_4:Eu^{3+}$ or 0.05 for bulk M- $LaPO_4:Eu^{3+}$. These observations indicate that the Eu^{3+} emission was likely enhanced by an energy transfer process.