Supporting Information

Morphology Controllable Synthesis of $NaLa(WO_4)_2$: Morphology Dependent Photoluminescent Property and Single-phased White Light Emission of $NaLa(WO_4)_2$: $Eu^{3+}/Tb^{3+}/Tm^{3+}$

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Hydrothermal Synthesis of $NaLa(WO_4)_2$ Microplates. Na_2WO_4 stock solution was prepared by dissolving $Na_2WO_4\cdot 2H_2O$ (0.660 g, 2 mmol) in 25 mL distilled water. The obtained Na_2WO_4 stock solution was then added dropwise into a well-stirred mixture of $La(NO_3)_3$ (1 mmol, 5 mL) and EDTA-2Na (0.010 g, 0.050 g or 0.100 g) at room temperature. Additional 18 mL distilled water was added into the resultant white suspension. The pH value of the reaction system was adjusted to about 8.0 by using NaOH (3 M) and HCl (3 M) aqueous solutions. The white suspension was stirred for another 30 min and then transferred into a 60-mL Teflon-lined stainless autoclave. The autoclave was tightly sealed and maintained at 200°C for 24 h, then cooled naturally to room temperature. The resulting precursor was collected by centrifugation, washed with distilled water for several times, and finally dried at 60°C for 24 h. The final product was obtained by calcining the resulted precursor at 600°C for 2 h in air with a heating rate of 5 °C/min. According to the amount of EDTA-2Na added in the reaction system, the samples were denoted as **S2, S3** and **S4** respectively.

In addition, when the pH values of the corresponding precursor solutions were not adjusted, samples **S2′**, **S3′** and **S4′** were also prepared for comparison.

Hydrothermal Synthesis of $NaLa(WO_4)_2$ Connected Twin-microspheres and Submicrodumbbells. Stock solution A was prepared by dissolving 0.379 g (1 mmol) $La(NO_3)_3$ and 0.100 g EDTA-2Na in 10 mL ethanol. Stock solution B was prepared by dissolving 0.660 g (2 mmol) $Na_2WO_4\cdot 2H_2O$ in 12 mL or 6 mL distilled water. Then, stock solution B was added dropwise into well-stirred stock solution A. An extra amount of 14 mL or 20 mL ethanol was added into the reaction system. The resultant white suspension was allowed to stir for another 30 min before it was transferred into a 60-mL Teflon-lined stainless autoclave which was filled up to 60% capacity. The autoclave was tightly sealed and maintained at 200°C for 24 h, then cooled naturally to room temperature. The resulting precipitate was collected by centrifugation, washed with distilled water for several times, and finally dried at 60°C for 24 h. According to the different volumes of water and ethanol used in the reaction system, the samples were denoted as **S5** and **S6**, respectively.

Hydrothermal Synthesis of $NaLa(WO_4)_2$ Nanocrystals. Stock solution A was prepared by dissolving 0.379 g (1 mmol) $La(NO_3)_3$ and 0.500 g PVP in 30 mL ethanol. Stock solution B was prepared by 0.660 g (2 mmol) $Na_2WO_4 \cdot 2H_2O$ in 5 mL distilled water. Then, stock solution B was added dropwise into well-stirred stock solution A. The resultant white suspension was allowed to stir for another 30 min before it was transferred into a 60-mL Teflon-lined stainless autoclave. The autoclave was tightly sealed and maintained at 200°C for 24 h, then cooled naturally to room temperature. The resulting precipitate was collected by centrifugation, washed with distilled water for several times, and finally dried at 60°C for 24 h. The sample was denoted as **S7**.

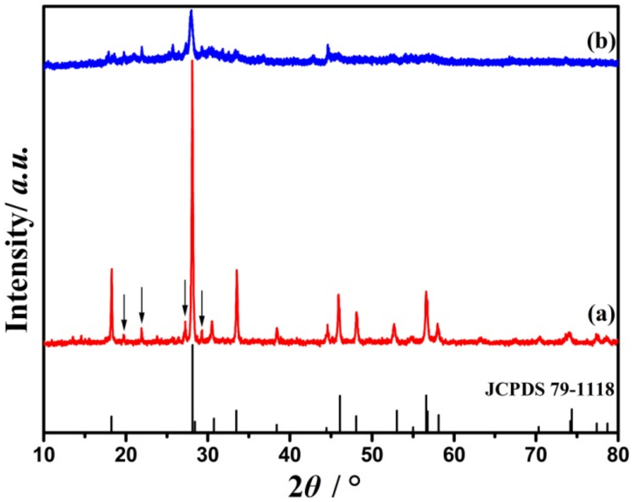

Figure S1. XRD patterns of $NaLa(WO_4)_2$ samples: the precursor of **S1** (a), and **S2** (b). The standard data for tetragonal $NaLa(WO_4)_2$ (JCPDS card 79-1118) is also presented at the bottom for comparison.

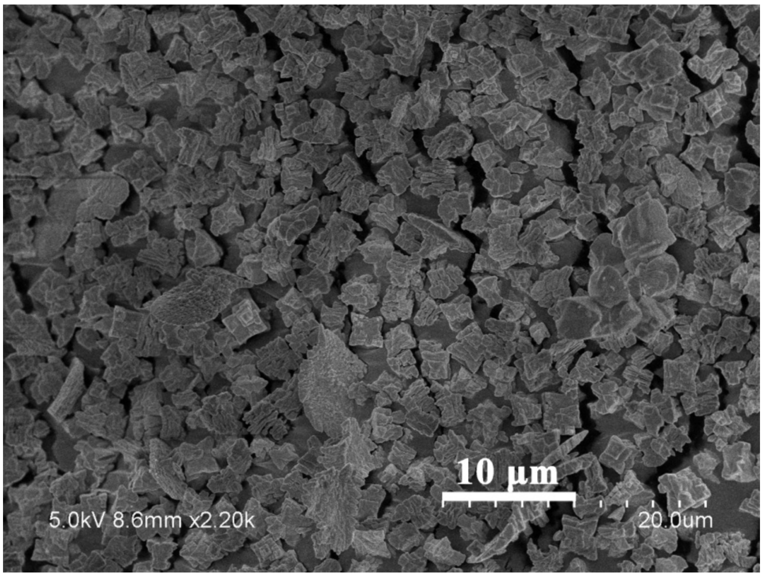

Figure S2. SEM image of $NaLa(WO_4)_2$ synthesized without addition of any additives.

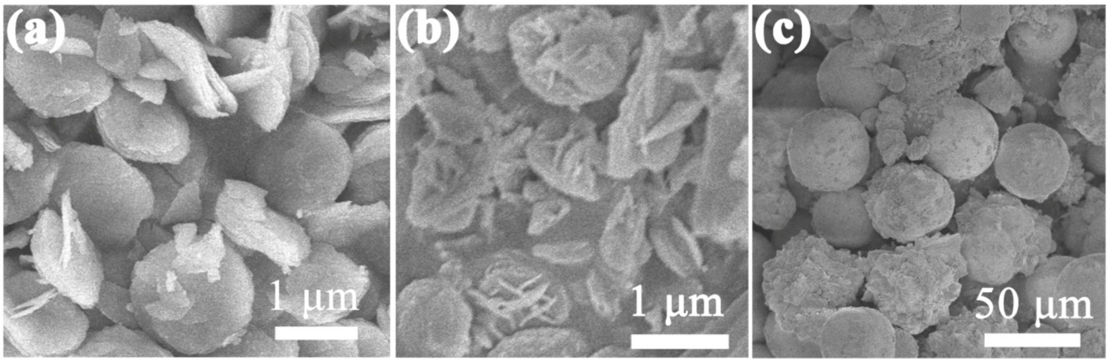

Figure S3. SEM images of (a) **S2′**, (b) **S3′** and (c) **S4′** when the pH values of their precursor solutions were not adjusted.

Table S1. pH value on increasing the amount of EDTA-2Na and morphology change in comparison with **S2-S4**.

sample	The mass of EDTA-2Na	pH value of the precursor solution without adjustment	Morphology change
S2′	0.010 g	*ca.* 7.7	No change
S3′	0.050 g	*ca.* 7.3	Change a lot
S4′	0.100 g	*ca.* 6.9	Completely change

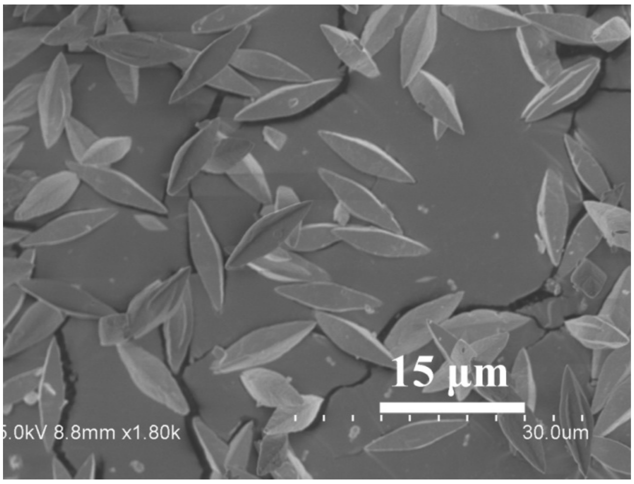

Figure S4. SEM image of $NaLa(WO_4)_2$: 1.5 mol% Eu^{3+}/ 4 mol% Tb^{3+}/ 3 mol% Tm^{3+}.

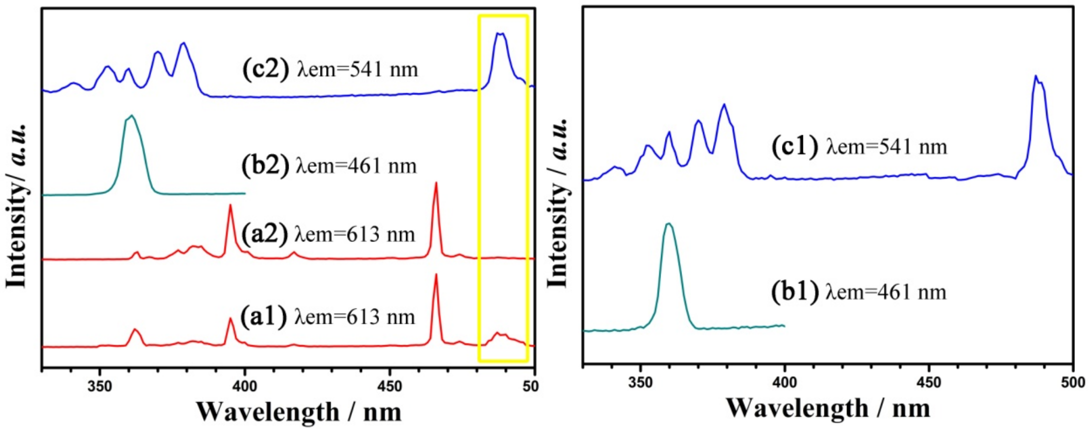

Figure S5. Excitation spectra of NaLa(WO_4)$_2$: 1.5 mol% Eu^{3+}/ 4 mol% Tb^{3+}/ 3 mol% Tm^{3+} microspindles: (a1) λem=613 nm; (b1) λem=461 nm; (c1) λem=541 nm. For comparison, the excitation spectra of NaLa(WO_4)$_2$: Ln^{3+} microspindles: (a2) Ln^{3+}= Eu^{3+}; (b2) Ln^{3+}= Tm^{3+}; (c2) Ln^{3+}= Tb^{3+} were also listed.

The excitation spectrum of the NaLa(WO_4)$_2$: 1.5 mol% Eu^{3+}/ 4 mol% Tb^{3+}/ 3 mol% Tm^{3+} measured by monitoring 613 nm emission of Eu^{3+} is shown in Figure S5, a1. A weak and broad peak located at 486 nm can be observed, and it cannot be attributed to any transitions of Eu^{3+}, when compared with the excitation spectrum of NaLa(WO_4)$_2$: Eu^{3+} (Figure S5, a2). While it can be attributable to the $^7F_6 \rightarrow {}^5D_4$ transition of Tb^{3+} (Figure S5, c2), which clearly demonstrates the energy transfer from Tb^{3+} to Eu^{3+}, and it is in accordance with the literature.[1] The excitation spectrum of NaLa(WO_4)$_2$: Eu^{3+}/Tb^{3+}/Tm^{3+} measured by monitoring 461 nm emission of Tm^{3+} is shown in Figure S5, b1, and it has no obvious differences with that of NaLa(WO_4)$_2$: Tm^{3+} (Figure S5, b2). It is the same thing with the excitation spectra of NaLa(WO_4)$_2$: Eu^{3+}/Tb^{3+}/Tm^{3+} (Figure S5, c1) and NaLa(WO_4)$_2$: Tb^{3+} (Figure S5, c2) measured by monitoring 541 nm emission of Tb^{3+}, which is consistent with the literature.[2] The above results indicate that there is no energy transfer from Eu^{3+}, Tb^{3+} to Tm^{3+} or Eu^{3+}, Tm^{3+} to Tb^{3+}.

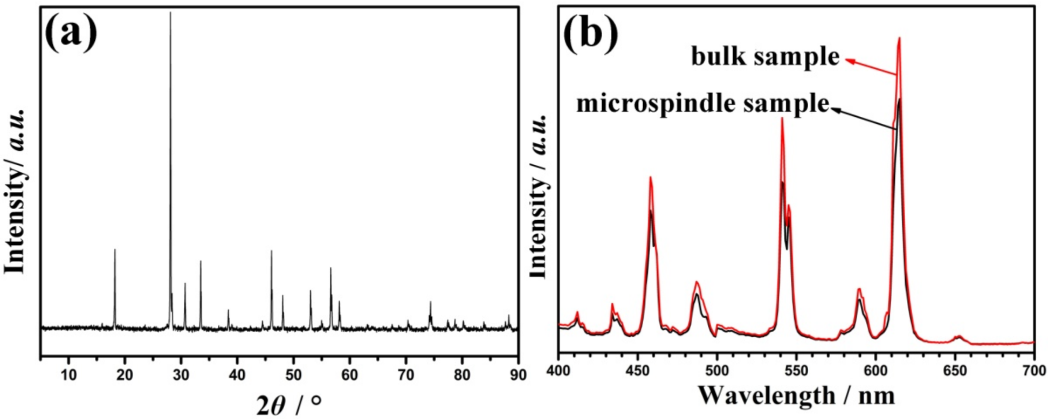

Figure S6. (a): XRD pattern of NaLa(WO$_4$)$_2$: 1.5 mol% Eu^{3+}/ 4 mol% Tb^{3+}/ 3 mol% Tm^{3+}; (b): The emission spectra of bulk NaLa(WO$_4$)$_2$: 1.5 mol% Eu^{3+}/ 4 mol% Tb^{3+}/ 3 mol% Tm^{3+} (red line) and the microspindle one (black line).

The bulk phosphor NaLa(WO$_4$)$_2$: 1.5 mol% Eu^{3+}/ 4 mol% Tb^{3+}/ 3 mol% Tm^{3+} were prepared by the conventional solid-state reaction in air. The starting materials lanthanium oxide (La$_2$O$_3$, 99.99%), europium oxide (Eu$_2$O$_3$, 99.99%), terbium oxide (Tb$_4$O$_7$, 99.99%), thulium oxide (Tm$_2$O$_3$, 99.99%), sodium carbonate (Na$_2$CO$_3$, analytical grade) and ammonium tungstate ((NH$_4$)$_{10}$W$_{12}$O$_{41}$, analytical grade) were weighed according to the desired stoichiometric ratio. After these powders were blended and grounded thoroughly in an agate mortar, the homogeneous mixture was calcined in an alumina crucible in a muffle furnace at a temperature of 900℃ for 10 h.[3]

The XRD pattern of NaLa(WO$_4$)$_2$: 1.5 mol% Eu^{3+}/ 4 mol% Tb^{3+}/ 3 mol% Tm^{3+} synthesized by solid-state reaction is shown in Figures S6a, and the crystal phase can be easily indexed to tetragonal NaLa(WO$_4$)$_2$, according to the standard data for tetragonal NaLa(WO$_4$)$_2$.

References

1. J. Wana, L.H. Cheng, J.S. Sun, *Journal of Alloys and Compounds*, 2010, **496**, 331–334.
2. D. Tu, Y.J. Liang, R. Liu, D.Y. Li, *Journal of Luminescence*, 2011, **131**, 2569–2573.
3. Q. Wei, D.H. Chen, *Optics & Laser Technology*, 2009, **41**, 783–787.