Electronic Supplementary Information

In situ immobilization of YVO_4:Eu phosphor particles on the film of vertically oriented $Y_2(OH)_5Cl\cdot nH_2O$ nanosheets

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Experimental details

Synthesis of Eu^{3+}-Doped Layered Yttrium Hydroxide Films on a Glass Slide Substrate.

The chemical bath deposition (CBD) method was employed to grow Eu^{3+}-doped layered RE hydroxychloride ($Y_{1.90}Eu_{0.10}(OH)_5Cl\cdot nH_2O$; LYH:Eu) nanosheets perpendicular to the substrate surface. Typically, the chemical bath solution was prepared by completely dissolving 9.5 mmol $YCl_3\cdot 6H_2O$ (ACROS ORGANICS, 99.9%), 0.5 mmol $EuCl_3\cdot 7H_2O$ (Sigma Aldrich, 99.9%), and 130 mmol NaCl (Alfa Aesar, 99.0%) in 100 mL deionized water under constant stirring. Hexamethylenetetramine (HMTA, 10 mmol, Sigma Aldrich, 99.0%) was used as a hydroxide source. Prior to the film deposition, the glass slide (2.5×7.5 cm^2) was immersed in acetone and degreased in an ultrasonic bath for 10 min, washed with copious ethanol, and then dried using an air gun. The cleaned glass substrate was tilted at an angle of ~ 45° in a 125 mL plastic bottle, in which the prepared solution was then slowly poured. The sealed bottle was ultrasonicated for 30 s to remove bubbles on the surface of the substrate. This chemical bath was held at 60 °C for 10 h in an oven. After the film growth was complete, the glass substrate was removed from the bath, washed with deionized water and ethanol successively, and dried with an air gun. The downward side of the substrate was used for all characterizations.

Immobilization of YVO_4:Eu Nanoparticles on the LYH:Eu Film of Nanosheets.

An aqueous *meta*-vanadate (VO_3^-) solution (10 mM) was prepared by dissolving the desired amounts of $NaVO_3$ (Sigma Aldrich, 98%) in distilled water. To immobilize in situ YVO_4:Eu particles on the edge of vertically oriented LYH:Eu hydroxide nanosheets, the obtained LYH:Eu films were immersed in 50 mL VO_3^- solutions for 1–5 h at room temperature with constant stirring (400 rpm). The solution pH was adjusted to ~7 and ~9 by drop-wise addition of the KOH solution to evaluate the pH dependence of the reaction rate and the size of the YVO_4:Eu particles. After the heterostructured YVO_4:Eu/LYH:Eu film formation was complete, the glass substrate was washed with deionized water and dried with an air gun.

Detection and Removal of Cu^{2+} Using YVO_4:Eu/LYH:Eu Films Grown on Glass Substrates.

A 1.0 M aqueous Cu^{2+} stock solution was prepared by dissolving $CuCl_2$ (Sigma

Aldrich, reagent grade) in deionized water at room temperature and then diluted to make 1.0 mM, 0.5 mM, and 30 μM test solutions. The sensitivity of the luminescence quenching of the YVO_4:Eu/LYH:Eu film to the Cu^{2+} concentration was assessed by separately putting a drop of these aqueous $CuCl_2$ solutions and deionized water on the same YVO_4:Eu/LYH:Eu film and drying in air. For the adsorption reaction of Cu^{2+} cations, the YVO_4:Eu/LYH:Eu film obtained at a pH of ~7 was dipped into 50 mL of the 30 μM aqueous $CuCl_2$ solution for 30 min at room temperature with constant stirring. The Cu^{2+}-adsorbed film was then washed with copious amounts of water and dried with an air gun.

Desorption of Cu^{2+} from YVO_4:Eu/LYH:Eu Films.

A 1.0 mM aqueous ethylenediaminetetraacetate (EDTA) solution was prepared by dissolving EDTA disodium salt dehydrate, $C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$ (TCI, 99.5%), in deionized water at room temperature. To evaluate the recyclability of the film after desorption of Cu^{2+}, the Cu^{2+}-adsorbed YVO_4:Eu/LYH:Eu film was immersed in 50 mL of 1.0 mM EDTA solution for 12 h at room temperature with constant stirring, rinsed with copious amounts of deionized water, and dried using an air gun. This adsorption/desorption reaction cycle was repeated twice to demonstrate the reversible luminescence quenching of the YVO_4:Eu/LYH:Eu film.

Characterizations

X-ray diffraction (XRD) patterns of the LYH:Eu and YVO_4:Eu/LYH:Eu films were recorded with a Bruker D8 Advance diffractometer using Cu-Ka radiation. Field emission scanning electron microscopy (FE-SEM) was carried out with a Carl Zeiss LEO SUPRA 55 scanning electron microscope operating at 30 kV. The excitation and emission spectra were recorded on an FP-6600 spectrophotometer (Jasco Corporation) with a Xenon flash lamp. Quantum yields of the obtained films were determined using an integrating sphere technique.

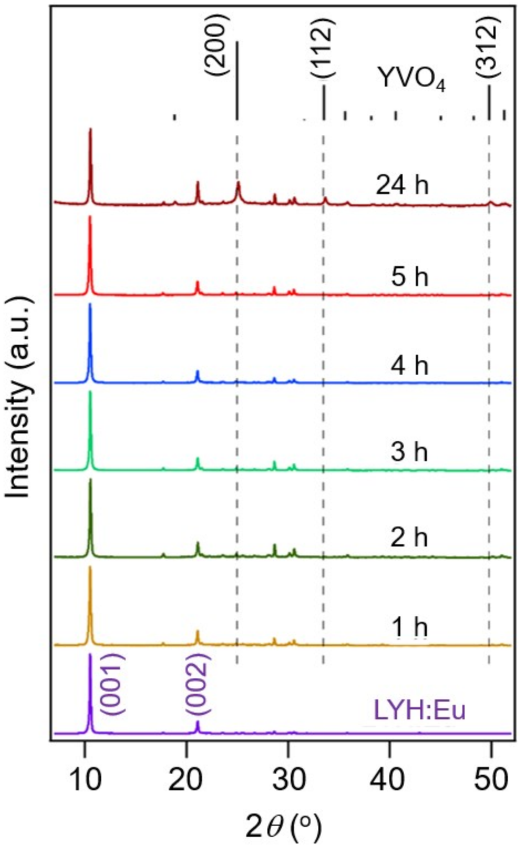

Fig. S1 X-ray diffraction patterns of the LYH:Eu film before and after reaction in a 10 mM aqueous $NaVO_3$ solution at room temperature, as a function of reaction time. Relative diffraction intensities of tetragonal YVO_4 (JCPDS No.17-0341) are also given for comparison. Based on XRD patterns, the essential formation reaction of YVO_4:Eu in this work is proposed by the equation: $Y_{1.90}Eu_{0.10}(OH)_5Cl{\cdot}nH_2O + 2VO_3^- \rightarrow 2Y_{0.95}Eu_{0.05}VO_4 + OH^- + Cl^- + (2 + n)H_2O$

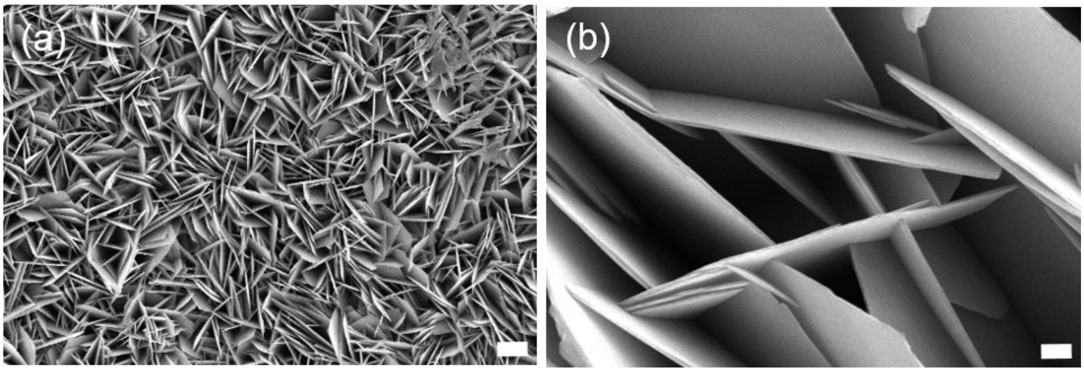

Fig. S2 SEM images of the as-grown LYH:Eu film. Scale bar = 2 μm (a) and 200 nm (b).

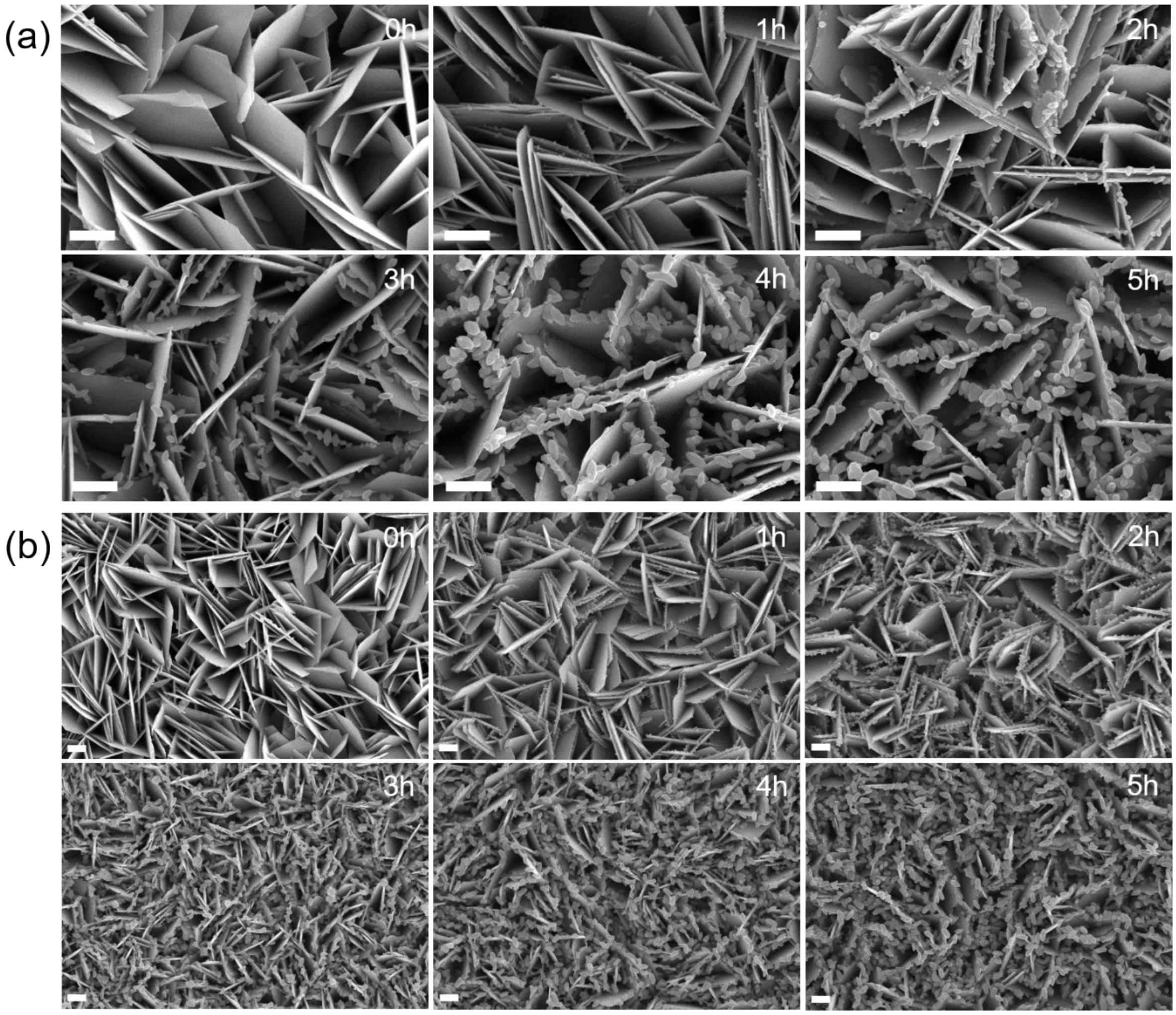

Fig. S3 (a) SEM images of LYH:Eu film as a function of reaction time in 10 mM aqueous $NaVO_3$ solution (scale bar = 1 μm) at room temperature. (b) Larger area images of corresponding films (scale bar = 1 μm).

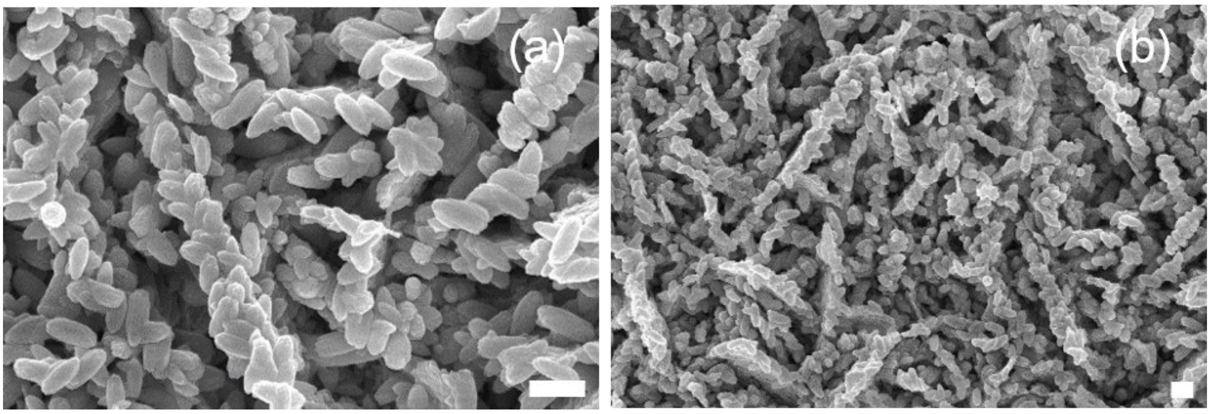

Fig. S4 (a) Small and (b) large area SEM images of LYH:Eu film after reaction in 10 mM aqueous $NaVO_3$ solution for 24 h (scale bar = 1 μm).

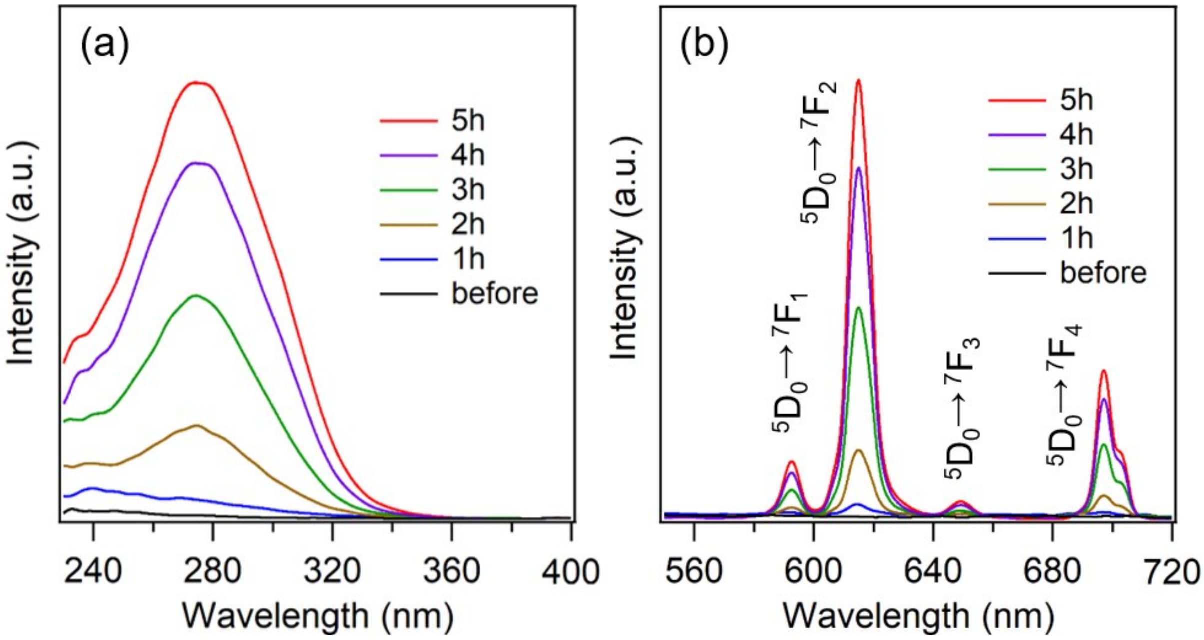

Fig. S5 (a) Excitation (λ_{em} = 615 nm) and (b) emission (λ_{ex} = 273 nm) spectra of LYH:Eu films before and after reaction in 10 mM aqueous $NaVO_3$ solution as a function of reaction time at room temperature.

As shown in Fig. S5a, when monitored at 615 nm, practically no absorption band was observed in the excitation spectra of the as-synthesized LYH:Eu film. Even the series of weak peaks generally observed in the 350–400 nm region, which are attributed to the intra-4f electronic transitions of Eu^{3+}, were not clearly distinguishable. The reaction of this film in a

$NaVO_3$ solution induced a significant increase in photoexcitation intensity as a function of reaction time. The highly enhanced, broad excitation band at ~273 nm is ascribed to charge transfer (CT) from the O^{2-} ligands to the central vanadium atom within the VO_4^{3-} group ions, indicating energy transfer from the CT band to the excited states of Eu^{3+} ions in the YVO_4 matrix.[S1] The emission spectra measured at an excitation wavelength of 273 nm showed the characteristic $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions of Eu^{3+}, with the dominant $^5D_0 \rightarrow {}^7F_2$ transition around 615 nm leading to the bright red emission of the YVO_4:Eu/LYH:Eu films (Fig. S5b). The strong increase in emission intensity, which was essentially the consequence of efficient energy transfer, was evidently caused by significant formation of YVO_4:Eu phosphor. Such a variation in the PL spectra of the LYH:Eu film was consistent with those observed in XRD patterns and SEM images, confirming the triggering of the conversion to YVO_4:Eu phosphor particles at its surface after 2 h reaction and the subsequent increase in size and number density of particles with increasing reaction time.

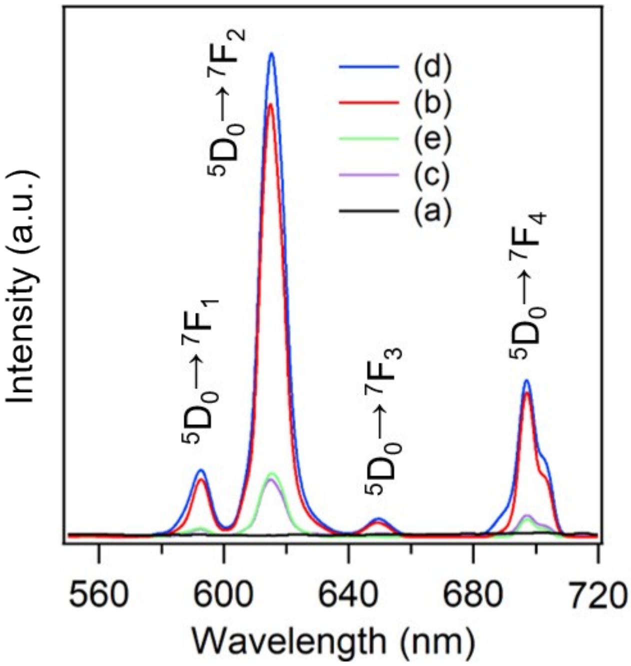

Fig. S6 Emission spectra under a 312 nm UV lamp of (a) the as-prepared LYH:Eu film, YVO_4:Eu-immobilized LYH:Eu film (b) before and (c) after the first reaction in 30 μM aqueous Cu^{2+} solution for 30 min. YVO_4:Eu-immobilized LYH:Eu film (d) after regeneration in 1.0 mM EDTA solution for 12 h and (e) after the second adsorption reaction in 30 μM aqueous Cu^{2+} solution for 30 min.

References

S1. K. Riwotzki and M. Haase, *J. Phys. Chem. B.*, 1998, **102**, 10129.