Enhanced Radioluminescence of $NaLuF_4:Eu^{3+}$ Nanoscintillators by Terbium Sensitization for X-Ray Imaging

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Luminescence yield (LY) calculation: c (ε) is the photon cross-section function obtained from the National Institute of Standard Technology (XCOM) database,[1] where ε is the corresponding photon energy, ρ is the scintillator density, and d is the thickness. Therefore, the X-ray attenuation coefficient (α) is defined as follows:

$$AE(\varepsilon,d) = (1 - e^{-c(\varepsilon)\rho d}) \times 100\% \tag{1}$$

$$AE(d) = \int_{1.15}^{69.6} \frac{AE(\varepsilon,d) \times R(\varepsilon)d\varepsilon}{\int_{1.15}^{69.6} R(\varepsilon)d\varepsilon} \tag{2}$$

In calculating the X ray attenuation efficiency as a function of thickness, the c (ε) value is required to absorb the entire X ray emission spectrum of the material. In Equation 3, R (ε) is the X-ray output spectrum of the X-ray tube (as shown in Figure 5a, operating voltage is 50 kV, unit keV). Finally, the calculated c (ε) is converted into formula 1 to obtain the thickness of AE function.

$$c(\varepsilon) = \int_{0}^{60} \frac{c(\varepsilon) \times R(\varepsilon)d\varepsilon}{(\int_{0}^{60} R(\varepsilon)d\varepsilon)} \tag{3}$$

The X-ray scintillator's light production was calibrated against the commercial LuAG:Ce scintillator (22,000 photons MeV^{-1}). The RL spectrum was measured by placing the LuAG:Ce sample in the same position as the reference scintillator. Light yield is defined as the ratio of the number of photons emitted by the luminous point to the total energy of the X-ray absorbed, and it represents the internal X-ray conversion efficiency. According to this definition, the photon count emitted by scintillators should be normalized to the same X-ray attenuation (100 %), as follows:

$$PC_{normalized} = \frac{PC_{measured}}{AE(d)} \tag{4}$$

$$LY_s = LY_{LUAG:Ce} \frac{PC_{normalized}(S)}{PC_{normalized}(LuAG:Ce)} \tag{5}$$

Then these RL spectra are integrated to obtain the corresponding photon counting results. Where, AE % is the X-ray attenuation efficiency (%) of scintillator of a certain thickness. Finally, the calculated parameters were substituted into formula 5 to obtain the corresponding Luminescence yield.

Calibration of minimum dose rate: The lowest limit detection dose rate (LOD) is an important index to judge whether a material can become an X-ray scintillator, that is, it has a good response to X-ray at a very low X-ray dose. The dose rate of the material was measured by tungsten and copper slices, and the working current of the X-ray excitation source (0-70 mA) was changed at the same time to adjust the radiation of the X-ray dose rate. The dose rate of the X-ray excitation source was calibrated for the two (the action of tungsten and copper slices and the change of current), and the results were linearly fitted to obtain the current-dose relationship after fitting. The photophysical test of rare earth nanocrystals under X-ray radiation was carried out by the action of tungsten plate and copper plate and the change of current, and the corresponding RL spectra were recorded. The luminescence intensity of the characteristic emission peak of the material was recorded in the fitted current dose relation. With the luminescence intensity of the characteristic emission peak as the vertical axis and the fitted dose as the horizontal axis, a curve was obtained. The linear fitting of the curve was carried out to obtain the relation $y = kx + b$, and the y value was taken as 3 times of the fluorescence intensity under the environmental background (that is, SNR = 3). The corresponding x value was calculated, and the x value was the lowest limit dose rate.

Modulation transfer function (MTF) calculation: The modulation transfer function is a parameter that characterizes the spatial resolution of the material imaging, defining the sum of the difference ratio between the maximum and minimum gray levels in the image. A customized thin tungsten sheet (1 mm) with a clear and sharp boundary was placed on the rare earth nanocrystalline film with an Angle of 10 ~ 20° between the tungsten sheet boundary and the scintillation film boundary. X-ray imaging images of the device were recorded under X-ray radiation. Import the obtained X-ray image with tungsten sheet into Matlab to get the edge diffusion function (ESF), differentiate the function to get linear diffusion function (LSF), and then perform Fourier transform on it. The calculation process can be seen as follows:

$$MTF\ (v) = F\ (LSF(x)) = \frac{d\ (ESF(x))}{dx} \tag{6}$$

In the equation, the parameter υ is the space frequency, χ is the pixel position, the derivative of the edge diffusion function is the LSF, and the Fourier transform function of LSF is the calculated MTF.

References

[1] M.J. Berger, J.H. Hubbell, S.M. Seltzer, J. Chang, J.S. Coursey, R. Sukumar, D.S. Zucker, K. Olsen, XCOM: photon cross sections database, XCOM: Photon Cross Sections Database | NIST, **2013**.

Table S1. The corresponding contents of rare earth atoms in nanoparticles doped with different content of Tb^{3+} through EDXA measurement.

Tb^{3+} (mol%)	**0**	**5**	**10**	**15**
F	74.10	74.60	74.00	73.50
Eu	2.05	2.16	1.89	2.14
Gd	1.95	1.34	0.62	
Tb		0.80	1.20	2.02
Lu	9.21	10.00	8.50	9.13

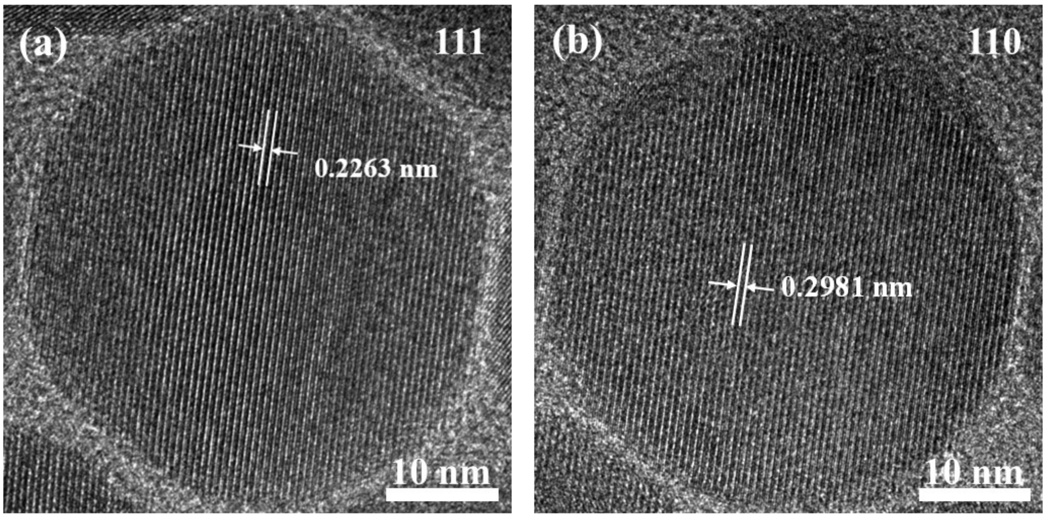

Fig. S1. HR-TEM image of the $NaLuF_4$:Gd/Tb/Eu (10/5/15 mol%).

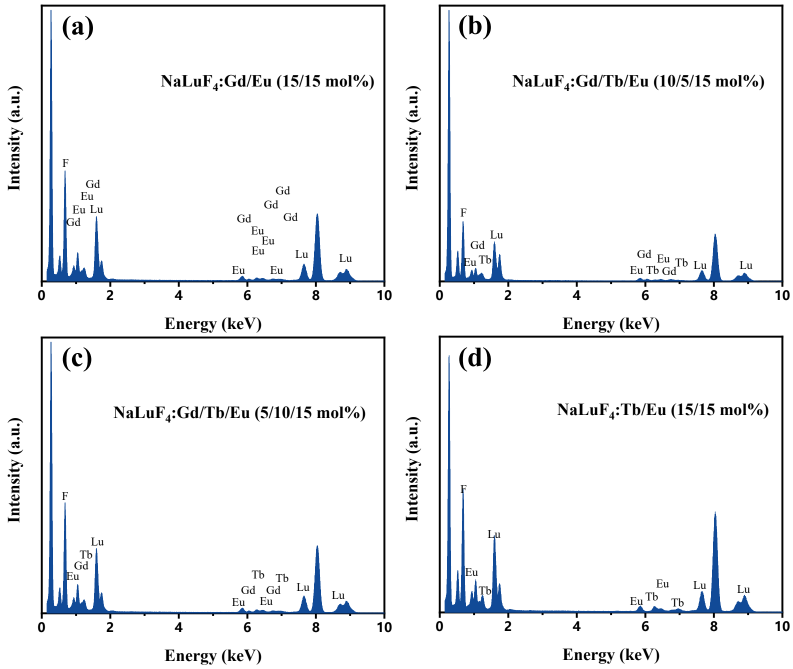

Fig. S2. EDXA spectra of NaLuF$_4$:Gd/Eu (15/15 mol%) (a), NaLuF$_4$:Gd/Tb/Eu (10/5/15 mol%) (b), NaLuF$_4$:Gd/Tb/Eu (5/10/15 mol%) (c), and NaLuF$_4$:Tb/Eu (15/15 mol%) (d) nanocrystals. Corresponding stoichiometric composition of NaLuF$_4$:Gd/Tb/Eu (x/y/15 mol%; x = 0-15) nanocrystals.

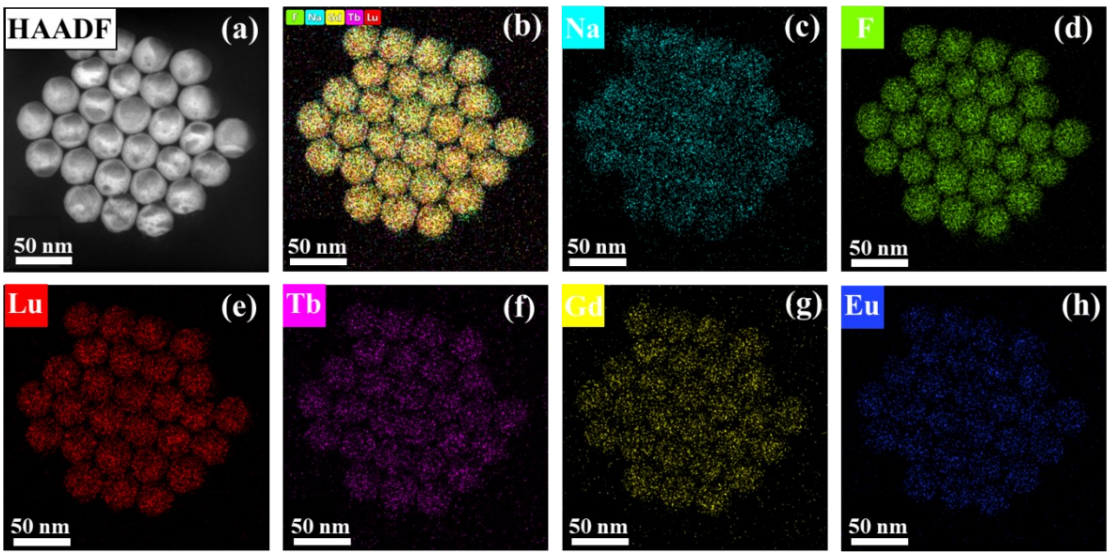

Fig. S3. (a) HAADF-STEM image of the as-synthesized NaLuF$_4$:Gd/Tb/Eu (10/5/15 mol%) nanoparticles. (b-k) Energy-dispersive X-ray element mapping of as-prepared NaLuF$_4$:Gd/Tb/Eu (10/5/15 mol%) nanocrystals (Na, blue; F, green; Lu, red; Tb, purple; Gd, yellow; Eu, dark blue).

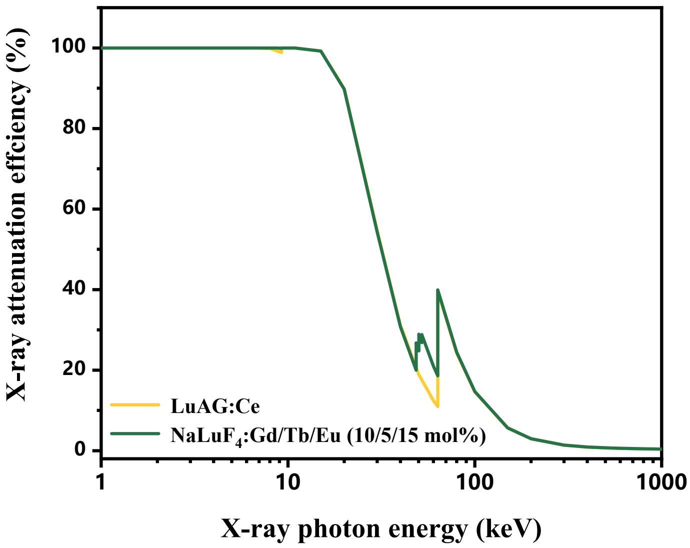

Fig. S4. Calculated X-ray attenuation efficiency spectra of LuAG:Ce and $NaLuF_4$:Gd/Tb/Eu (10/5/15 mol%) nanoparticles.

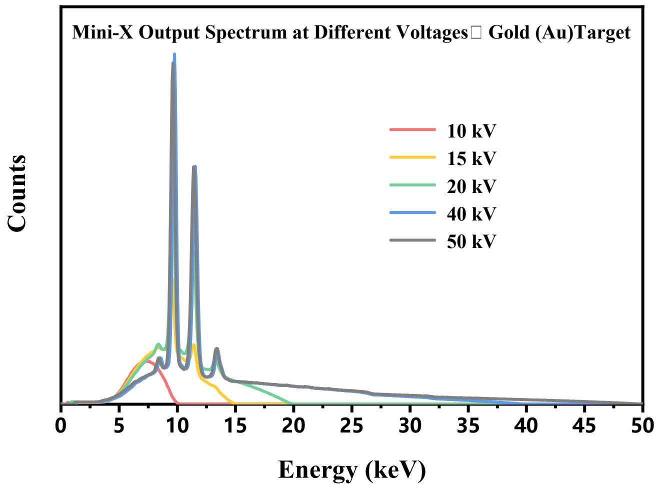

Fig. S5. Emission spectra of Mini-X2 at different voltages.

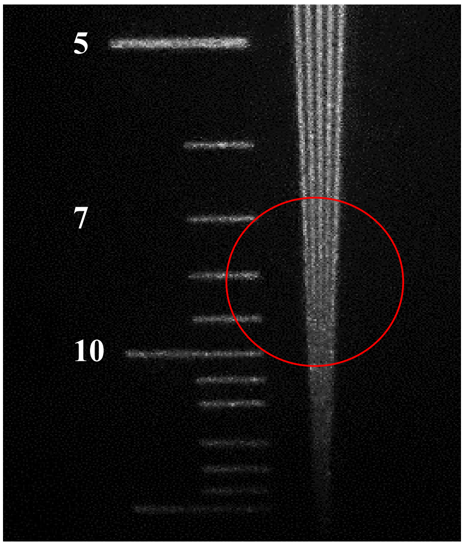

Fig. S6. X-ray image of the standard X-ray test pattern plate based on $NaLuF_4$:Gd/Tb/Eu (10/5/15 mol%) nanocrystals scintillator screen.

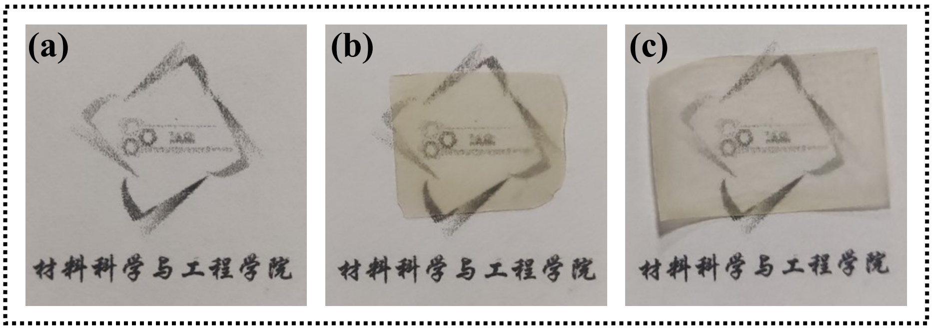

Fig. S7. Verify transparency: (a) print the artwork; digital photograph of scintillation film covered on the printed original image, (b) film containing $NaLuF_4$:Gd/Tb/Eu (10/5/15 mol%) nanocrystal and (c) without nanocrystals.