Enhancement of Eu$^{3+}$ Emission in YVO$_4$:Eu$^{3+}$ Nanocrystals by Li$^+$ Codoping: An Oxidant-Resistant Dispersion and Polymer Film

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Supporting Information

ABSTRACT: The enhancement of red emission of YVO$_4$:Eu$^{3+}$ nanocrystals by Li$^+$ codoping has been achieved. The effect of Li$^+$ codoping on the crystalline properties and the luminescence of Eu$^{3+}$ has been thoroughly studied. An increase of the unit cell volume and crystallinity of the nanocrystals is observed as the concentration of Li$^+$ codoping increases. The lattice expansion could be related to occupation of the interstitial sites by the Li$^+$ ions. The nanocrystals appear to be assemblies of rodlike nanostructures along with cubic-shaped rough nanostructures of uniform size. The optimum concentration of Li$^+$ codoping for luminescence enhancement is found to be 5 at. % at which Eu$^{3+}$ emission is increased by about 2.5 times. The fall in Eu$^{3+}$ emission after codoping of Li$^+$ (7–15 at. %) is observed. Is it the increased crystallinity (i.e., the size) or the lattice expansion that poses a limit to luminescence enhancement? Annealing at 500 and 850 °C increased the luminescence emission by threefold and fivelfold, respectively. The samples are readily dispersible in deionized water and incorporated easily in the flexible polymer film made of polyvinylidene fluoride. The dispersion-in-water shows bright red luminescence as low as 50 μg/mL. The emission intensity of the dispersion decreases linearly with concentration with a slope almost equal to unity. The dispersion and the flexible film do not show luminescence degradation under the influence of oxidizing H$_2$O$_2$ medium. The oxidant-resistant nature with enhanced luminescence could serve as a suitable red emitter for lighting and display applications.

INTRODUCTION

Lanthanide-doped inorganic luminescent materials have been extensively studied for applications in optoelectronics as well as biomedical applications including drug delivery and optical and magnetic imaging.1,2 The lanthanide-based inorganic nanoparticles are preferentially studied over the organic dyes, lanthanide chelates, and quantum dots because of the fact that the latter exhibited short luminescence lifetime, poor photostability, intermittent blinking, and potential long-term toxicity issues.3–5 Further, the inorganic nanoparticles have several advantages—high chemical and photostability, narrow emission bandwidths, large Stokes shift, absence of blinking, and long luminescence lifetime of the Ln$^{3+}$ ions, which is highly desirable for sensitivity and bioimaging; the inorganic host provides a steady microenvironment for the Ln$^{3+}$ emitters; low cytotoxicity as the host matrix trapped the Ln$^{3+}$; and tunability of the Ln$^{3+}$ emissions by designing the morphology and composition of the host material.6–7 It is necessary that the Ln$^{3+}$-doped luminescent nanomaterials be improvised to yield better emission efficiency, longer lifetime, and excellent photostability. Therefore, the choice of the material and devising a method to enhance luminescence outcome is of paramount importance. In this context, yttrium orthovanadate (YVO$_4$) is an inorganic mixed metal oxide of great significance. It is a self-activated blue emitting phosphor extremely beneficial for lanthanide ion-activated luminescent materials which has found potential applications in cathode ray tubes, solid state lasers, fiber-optics, H$_2$O$_2$ sensors, upconversion luminescence, bioimaging as well as red-emitting optical guide for magnetic fluid hyperthermia, etc.8–10 Further, it has good thermal stability, low susceptibility to moisture, excellent mechanical, physical and birefringence properties. It possess high down-conversion efficiency owing to low phonon energy (2.8188 × 10$^{-21}$ J).16 Trivalent europium (Eu$^{3+}$) ions are excellent activators for red light generation in the YVO$_4$ matrix since there is strong VO$_4$$^{3−}$–Eu$^{3+}$ energy transfer via exchange interaction which is favored by the overlapping of wavefunctions and the V–O–Eu bond angle of 170°.17–19 There are also reports on methods to enhance the luminescence emission such as codoping with certain metal (mono-, di- or tri-valent) ions in appropriate stoichiometry, tuning of synthetic parameters and morphological variations.20–24 The enhancement is effective when the codopant acts as a sensitizer or improves the crystallinity of the materials. The codoping of

Received: May 2, 2019
Accepted: July 23, 2019
Published: August 15, 2019

DOI: 10.1021/acsomega.9b01265
ACS Omega 2019, 4, 13762−13771
Li⁺ in the YPO₄:Dy³⁺ system has improved the crystallinity and emissions of Dy³⁺ including its near infrared band at 872 nm. The presence of Ce³⁺ increased the probability of non-radiative energy transfer toward the activator in the GdPO₄:Tb³⁺ systems owing to its sensitization effect. It was suggested that the introduction of a small fraction of impurity metal ions into a codopant lattice induces fast energy transfer from the host to activator ions. Based on the above facts, it is anticipated that Li⁺ codoping in the YVO₄:Eu³⁺ system could, therefore, yield a potential bright red emitting material for display and lighting devices as well as bioimaging applications.

In this article, we report the synthesis of YVO₄:5Eu³⁺, Li⁺ nanocrystals of uniform size by a hydrothermal method using a water–glycerol (2:1 v/v) mixture as the solvent. YVO₄:5Eu³⁺ refers to 5 at. % Eu³⁺-doped YVO₄. The use of glycerol can serve as a reaction medium as well as a capping agent to prevent agglomeration and control the formation of nanocrystals. Li⁺ codoping is found to enhance the luminescence emission. The emissions from 5Dₐ→7Fᵣ of Eu³⁺ can be improved significantly after annealing at 500 and 850 °C. Luminescent YVO₄:Eu³⁺,Li⁺ nanocrystals were incorporated into a flexible polymer film. The robustness of the polymer film and dispersion-in-water toward oxidation is studied after the particles are dispersed in H₂O₂ media. The enhanced emission and resistance to oxidation showed that the materials can be promising for applications in display devices.

**Experimental Section**

**Materials.** Yttrium oxide (Y₂O₃, Sigma-Aldrich), europium oxide (Eu₂O₃, Sigma-Aldrich), ammonium metavanadate (NH₄VO₃, Sigma-Aldrich), lithium nitrate (LiNO₃, Sigma-Aldrich), sodium hydroxide (NaOH, Merck), and glycerol (Merck) are used as received for the synthesis of materials without further purification.

**Synthesis of YVO₄:5Eu³⁺,xLi⁺ (x = 0–15 at. %) Nanocrystals.** The percentage of Eu³⁺ ion doping is 5 at. % and Li⁺ doping is 1–15 at. %. The Eu³⁺ (5 at. %)-doped YVO₄ sample is denoted as YVO₄:5Eu³⁺. In a typical preparation, stoichiometric proportions of Y₂O₃, Eu₂O₃, and LiNO₃ are first dissolved in concentrated HNO₃ to obtain their nitrates. Excess acid, if any, is removed by addition of water followed by evaporation to dryness three or four times. The salts are then dissolved in 40 mL of water–glycerol mixture (2:1 v/v). In another solution, stoichiometric amounts of NH₄VO₃ and NaOH are dissolved in 40 mL of water–glycerol mixture (2:1 v/v). The molar ratio of NH₄VO₃/NaOH is 1:5. The two solutions are mixed and stirred for about an hour. A clear transparent greenish solution is obtained. This clear solution is transferred to a 100 mL Teflon lined autoclave and placed in a preheated oven at 150 °C for 3 h. After cooling to room temperature automatically, the products are collected by centrifugation. The products are washed with water till the pH of the liquid becomes neutral and finally with acetone. The products are dried at 80 °C for further analysis. Heat treatment or annealing of samples is carried out at 500 and 850 °C, subjecting to heat for 2 h. Further, the samples are heated at 500 °C to study the effect of annealing treatment. The YVO₄:5Eu³⁺,5Li⁺ is again annealed at 850 °C.

**Preparation of Flexible Polyvinylidene Fluoride Polymer Films Containing YVO₄:5Eu³⁺,5Li⁺.** About 0.5 g of polyvinylidene fluoride (PVDF) is dissolved completely in the dimethylformamide solution with continuous stirring. After complete dissolution of the PVDF, 10 mg of the powder sample is added to the above PVDF solution and the mixture is sonicated for about 30 min to achieve uniform dispersion of the powder. Then, the dispersion is poured on a cleaned corning glass surface placed on a level surface and dried at 80 °C. Thus the flexible polymer film is peeled off slowly from the surface of the glass after drying.

**Characterization.** X-ray diffractometry is used to identify the crystal structure and phase purity of the synthesized materials. The diffraction pattern was recorded from 15 to 75° in 2θ degree at room temperature using a PANalytical (X’Pert Pro) X-ray diffractometer with Cu Kα (1.54060 Å) radiation with a Ni filter. The X-ray diffraction (XRD) patterns of the nanocomposites were obtained using Bruker D8 ECO ADVANCE. The average crystallite sizes for the nanoparticles were calculated from the most intense diffraction peak (200) using the Scherrer formula D = 0.9λ/βcosθ, where λ is the wavelength of the incident X-ray, β is the full width at half maximum (fwhm) in radian, and θ is the diffraction angle. The shape and size of the nanostructures of the samples were characterized by transmission electron microscopy (TEM) carried out using a JEM2100 (JEOL) transmission electron microscope.
The nanocrystals are increased with the increase in the Li+-codoping concentration. Table 1 presents the calculated lattice parameters, peak positions of the (200) Bragg peak, fwhm, crystallite size and crystallinity of the Li+-codoped YVO₄:Eu³⁺ nanocrystals. The volumes of the unit cell of YVO₄:Eu³⁺, 10, and 15 at. % Li+-codoped nanocrystals are 27, 38, 46, and 54 nm, respectively. It is to be noted that the calculated crystallite size (D) may not give a true picture of the size of nanocrystals but it may apparently suggest the fact. Consequently, the decrease of fwhm as well as the increase of calculated crystallite size and crystallinity could have indicated the favorable growth of the particle size as the concentration of Li⁺ is increased.

The XRD patterns of the as-prepared 500 and 850 °C annealed YVO₄:Eu³⁺, SLi⁺ samples are shown in Figure S1 (Supporting Information). It is obvious that the annealing does not affect the tetragonal phase of YVO₄ in these samples. However, the intensity and the fwhm values of the peaks increase slightly. The increase in intensity could be due to increased crystallinity of the sample on removal of the organic molecule and OH/H₂O adsorbed on the nanoparticles. The removal of the OH/H₂O is also reflected in the corresponding infrared spectra of the samples. The fwhm values for the as-prepared 500 and 850 °C annealed YVO₄:Eu³⁺, SLi⁺ samples are 0.23°, 0.26°, and 0.33°, respectively. There can be two possible reasons for the slight broadening of the diffraction peaks after annealing: (a) decreased crystallite size, and (b) increasing lattice strain. The decrease of the crystallite size is not likely to occur since there is an increase of peak intensities after annealing. As the crystallinity increases, it is expected that the sharpness of the peak would also increase. Therefore, the peak broadening could be ascribed to the increase of the lattice strain in the nanoparticles as the annealing treatment transformed the morphology of the nanoparticles due to reduction of the amorphous behavior and assuming a nearly single crystalline nature.

Table 1. Calculated Lattice Parameters, Peak Positions of the (200) Bragg Peak, fwhm, Crystallite Size and Crystallinity of the Li⁺-Codoped YVO₄:Eu³⁺ Nanostructures

| lattice parameters | sample | a (Å) | c (Å) | V (Å³) | peak position (θ, x) | fwhm (2θ) | crystallite size (D) | crystallinity (C) |
|--------------------|--------|-------|-------|--------|---------------------|-----------|-------------------|-------------------|
| YVO₄:5Eu³⁺        | 7.134  | 6.285 | 319.85| 24.932 | 0.326               | 27        | 0.40              |
| YVO₄:5Eu³⁺,SLi⁺   | 7.138  | 6.291 | 320.50| 24.912 | 0.229               | 38        | 1.15              |
| YVO₄:5Eu³⁺,10Li⁺ | 7.139  | 6.291 | 320.68| 24.872 | 0.192               | 46        | 1.95              |
| YVO₄:5Eu³⁺,15Li⁺ | 7.139  | 6.295 | 320.91| 24.756 | 0.163               | 54        | 3.19              |

microscope. For TEM measurements the samples were ground and dispersed in propan-2-ol. A drop of the dispersed particles was placed over a carbon coated copper grid and evaporated to dryness at room temperature. The photoluminescence spectra and decay curves were recorded using a Hitachi F-7000 FL spectrophotometer equipped with a 150 W Xe discharge lamp. All the measurements were performed at room temperature.

## RESULTS AND DISCUSSION

**XRD, TEM and Fourier Transform Infrared Study.**

Crystal structure and phase purity of YVO₄:5Eu³⁺, xLi⁺ (x = 0–15 at. %) nanocrystals have been determined by the XRD method. Figure 1a shows the XRD patterns of YVO₄:5Eu³⁺, xLi⁺ (x = 0, 5, 10 and 15 at. %) nanocrystals. The diffraction peaks of the samples can be indexed as a pure tetragonal phase (space group 14/amd and Z = 4) in agreement with the standard JCPDS no. 17-0341. As shown in Figure 1b, the peak positions of (200) planes are also shifted to a slightly lower 2θ as the concentration of Li⁺-codoping is increased. According to Bragg’s law of diffraction, the position of the diffraction peak of the diffraction angle is inversely related to the d-spacing. Therefore, the shift toward the lower diffraction angle indicates an increase in the d-spacing. The calculated lattice parameters, fwhm (fwhm in 2θ), crystallite sizes and crystallinity of the 0, 5, 10 and 15 at. % Li⁺-codoped samples are presented in Table 1. The volumes of the unit cell of the nanocrystals are increased with the increase in the Li⁺-codoping concentration. Here, we can obtain valuable information about the crystalline properties of the nanocrystals. At coordination number 6, the ionic radii of Y³⁺, Eu³⁺, and Li⁺ are 0.90, 0.94, and 7.60 pm, respectively. The size of the Li⁺ ion is smaller than that of the Y³⁺ ion. It is expected that the unit cell volume will be decreased when Li⁺ substitutes the Y³⁺ sites in these nanocrystals. But, the actual volume is increased with Li⁺ substitution. The sample YVO₄:5Eu³⁺ has a = 7.133 Å, c = 6.285 Å, and V = 319.85 Å³, whereas YVO₄:5Eu³⁺,10Li⁺ has a = 7.139 Å, c = 6.291 Å, and V = 320.68 Å³. This could suggest that Li⁺ occupies the interstitial sites rather than the Y³⁺ lattice sites similar to that in YPO₄:Eu³⁺ as reported by Parchur et al. In Figure 1c, the variation of the fwhm and unit cell volumes are presented. The fwhm values are decreased with increasing Li⁺ ion codoping. This is an indication of the increase of crystallinity of the nanocrystals as the concentration of Li⁺ is increased. The relative extent of crystallinity (χc) can be calculated by using an empirical relation between χc and β(hkl), that is, β(hkl) × √χc = Kω, where β(hkl) is fwhm (in degrees) of the most intense peak and Kω is a constant (0.24). The crystallinity of the Li⁺-codoped YVO₄:Eu³⁺ samples are increased from 0.40 to 3.19 as shown in Table 1 with the increase of Li⁺ doping. Meanwhile, the calculated crystallite size obtained for the 0, 5, 10, and 15 at. % Li⁺-codoped nanocrystals are 27, 38, 46, and 54 nm, respectively.
the range of 100° indicates the enhancement of crystallinity of the sample after the change in the sizes of the nanoparticles after annealing at 850°. Prepared and annealed (500 and 850°) samples are shown in Figure S3. All the spectra contain two main absorption bands in the 400–1000 cm−1 region— a weak one at 451 cm−1 corresponds to the antisymmetric bending ν4 mode (A2u) originating from the Y–O vibration and an intense broad band covering 550–1000 cm−1 centered at 781 cm−1 corresponding to symmetric stretching ν3 (A2u + E_u) originating from the V–O vibration of the VO4 group.25 The other vibrational bands in the 1000–4000 cm−1 range are assigned to C–O stretching (1064 cm−1), O–H bending (1644 cm−1), CH2 deformation (1359 and 1477 cm−1), and O–H stretching (3360 cm−1).30,31 In a peculiar manner, the intensity of the bands due to the O–H groups is diminished with increasing annealing temperatures. This could be ascribed to the loss of O–H and H2O adsorbed on the nanoparticles. However, the bands due to C–O and CH2 groups do not show any significant decrease in the intensity for 500° annealing. When it is annealed at 850°, the C–O and CH2 bands are also diminished which implies the partial removal of the solvent (glycerol) from the surface of the nanoparticles.

Photoluminescence Study. Figure 4a shows the excitation spectra of the as-prepared, 500 and 850°C annealed samples of YVO4:5Eu3+,5Li+ when the emission wavelength is monitored at 618 nm. Here, a strong excitation band is observed broadly in the 230–350 nm regions. The broad excitation band consists of peaks at 275 (shoulder) and 315 nm which are due to O–V CT transitions. These transitions arise from the transition of O2− (2p) → V5+ (3d) orbitals in the VO4 unit. According to the molecular orbital theory, the two peaks of CT transitions in the VO4 group namely at 275 and 320 nm are due to 1A2(4T1) (ground state) → 1E(4T2), 1B1(4E) (excited states) transitions.19 The low intensity bands in the 360–410 nm region of wavelengths correspond to f–f transitions of the Eu3+ ion.32 Figure 4b shows the emission spectra of the as-prepared YVO4:5Eu3+ sample after excitation at 320 and 395 nm. Compared to direct excitation at 395 nm, the emission intensity of Eu3+ (618 nm) on excitation at 320 nm is about 4-fold higher. The low emission intensity on direct excitation is due to the Laporte forbidden nature of f–f transitions. Emissions from Eu3+ are displayed, whereas no significant emission from the host can be observed. This indicates an efficient energy transfer from the host VO4− to Eu3+ ion. Figure 4c shows the emission spectra of the YVO4:5Eu3+,5Li+ (x = 0–15 at. %) samples after excitation at 320 nm. The emission intensity of Eu3+ increases up to 5 at. % of Li+ codoping and then decreases with increasing concentration of the Li+ ion. Beyond 5 at. % Li+ codoping, the emission intensities show a decrease. The inset shows the integrated area intensities of the 618 nm emission when the samples are excited at 320 nm. It is observed that the integrated area is maximum in 5 at. % Li+ codoping. However, no significant change of peak positions is observed. The change will be large when the 4f energy levels of Eu3+ are strongly affected by the crystal field. It is already established that the Eu3+ ion is highly useful in probing its site symmetry or crystal environment.33 The intensity ratio I(D5/2−F7/2)/I(D7/2−F5/2) is a determining factor of the Eu3+ site symmetry. In a highly symmetrical environment, the intensity value is close to 1 whereas if Eu3+ is located in a low symmetry site, the ratio approaches 10. In this work, for excitation at 320 nm, the ratio

Figure 2. (a–c) TEM and (d) HRTEM images of YVO4:5Eu3+,5Li+ nanocrystals. The inset of (c) shows the SAED pattern.
is in the range of 6.3−5.4 and for direct excitation at 395 nm, the ratio is in the range of 7.1−5.6. The ratio is decreased with increasing Li+ (x = 0−15 at. %) concentration. This implies that the site symmetry of Eu3+ is lowered on codoping with the Li+ ion.

The emission spectra of the YVO4:5Eu3+,xLi+ after excitation at 320 nm are shown in Figure 4d. Similar to the 320 nm excitation, the maximum emission is observed for the 5 at. % Li+ codoping. Here, the increase in the luminescence emission intensity of Eu3+ is lowered on codoping with the Li+ ion.

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The emission spectra of the YVO4:5Eu3+,xLi+ (x = 0−15 at. %) after excitation at (c) 320 nm, and (d) 395 nm. The inset (c) shows the integrated area intensity with Li+ concentration.

Figure 4. (a) Excitation spectra of the as-prepared YVO4:5Eu3+. (b) Emission spectra of YVO4:5Eu3+ after excitation at 320 and 395 nm. Emission spectra of YVO4:5Eu3+,xLi+ (x = 0−15 at. %) after excitation at (c) 320 nm, and (d) 395 nm. The inset (c) shows the integrated area intensity with Li+ concentration.

Figure 5. (a) Excitation and (b) emission spectra of the as-prepared, 500 and 850 °C annealed YVO4:5Eu3+,5Li+ samples.

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as-prepared samples, the emission intensity of Eu$^{3+}$ increases for the Li$^+$-codoped YVO$_4$:Eu$^{3+}$ sample. After annealing at 500 and 850 °C, the intensity ratio of the 5D$^0$ → 7F$^2$ and 5D$^0$ → 7F$^1$ transitions lies in the range of 6.2–5.4 for increasing Li$^+$ concentration, which is very similar to those of the as-prepared samples. The intensity ratios are 5.54, 6.11, and 6.25, respectively. This could suggest that the site symmetry of Eu$^{3+}$ is lowered slightly after annealing.

**Decay of the 5D$^0$ Level of Eu$^{3+}$**

For any luminescent system which follows the monoexponential or one lifetime component decay process, it can be expressed as log$_{10}$ $I$ = log$_{10}$ $I_0$ – ($t$/$\tau$)$/2.303$. Figure 6a,b show the plot of log$_{10}$ $I$ (I = intensity at time t) versus time (t) for the YVO$_4$:SEu$^{3+}$,SLi$^+$ (as-prepared, 500 and 850 °C annealed) sample after excitation at 320 and 395 nm, respectively. The logarithmic plots can be fitted linearly and the emission pathways follow first order exponential decay. Since for excitation at 320 nm, the decay of the 5D$^0$ level of Eu$^{3+}$ involves energy transfer from the host VO$_4$ to Eu$^{3+}$, the decay profile is fitted using the following non-exponential equation.

$$I = I_0 e^{(-t/\tau)-2be^{at}}$$

Here, $b$ is related to the energy transfer and diffusion coefficient. The equation has only one lifetime component, which is similar to the monoexponential profile. Figure 6c shows the luminescence decay profile of the 5F$^0$ level of Eu$^{3+}$ for the as-prepared, 500 and 850 °C annealed YVO$_4$:SEu$^{3+}$,SLi$^+$ samples after excitation at 320 nm. The emission is monitored at 618 nm. On 320 nm excitation, the excitation electrons undergo non-exponential decay (i.e., non-radiative energy transfer from VO$_4$ to Eu$^{3+}$). Here, the decay curves are fitted using the non-exponential eq 1 and the lifetimes are listed in Table 2. The

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Decay profile of the 5D$^0$ level of Eu$^{3+}$ for the as-prepared, 500 and 850 °C annealed YVO$_4$:SEu$^{3+}$,SLi$^+$ samples after excitation at (a,c) 320 and (b,d) 395 nm. The emission is monitored at 618 nm.
The lifetimes are longer for excitation at 320 nm compared to 395 nm. This is due to strong energy transfer from the host to the activator.

The decay profiles of the as-prepared YVO₄:5Eu³⁺, xLi⁺ (x = 0–15 at. %) and 500 °C-annealed YVO₄:5Eu³⁺, xLi⁺ samples for the excitation at 320 and 395 nm are presented, respectively, in Figures S5 and S6 (Supporting Information). Generally, for both the excitation wavelengths used, the lifetimes of the samples increase up to 5 at.% Li⁺ codoping. The lifetimes again decrease at 7 at.% Li⁺ codoping and then increase toward 15 at.% Li⁺ codoping. Their lifetime values are summarized in Table 2. Here, the lifetime values exhibit an increasing trend from 7 to 15 at.% Li⁺ codoping, but their emission intensities exhibit a decreasing trend. It is to be noted that, in the XRD pattern, the crystallinity increases as Li⁺ codoping increases. And the TEM images also revealed the favorable increase of particle size and enhanced crystallinity with Li⁺ doping. The increased crystallinity can have a positive influence on the efficiency of luminescence emission. The lifetime values also suggest increased population of the excited state of Eu³⁺ in the 7–15 at.% Li⁺-codoped samples. But the lifetime values are lower than the 5 at.% Li⁺-codoped sample. This could be the result of the relative position of Eu³⁺ in the nanocrystals with the increase of the particle size. There is also another possible speculated reason. The Li⁺ ion has 1s22s0 configuration, that is, the 2s orbital is completely vacant. As the Li⁺ pair may serve as a non-radiative trap to quench the luminescence of Eu³⁺ even though the population of the electrons excited may increase. As a result of these factors, the luminescence intensities of Eu³⁺ fall as the concentration of Li⁺ increases beyond 5 at.% codoping. The speculative reasoning may require further experimental studies.

**CIE Coordinates, Dispersion-In-Water and Flexible Polymer Film Formation.** The color tone of the emitted light can be understood by examining the CIE color coordinates. The CIE coordinates are obtained by using the lifetime values of the as-prepared YVO₄:5Eu³⁺ sample after excitation at 320 and 395 nm and are, respectively, 710 and 657 μs. Upon Li⁺ codoping, the lifetime of the sample is increased. Further on annealing, the lifetimes of the samples are also increased.

The as-prepared, 500 and 850 °C annealed YVO₄:5Eu³⁺, xLi⁺ samples have a lifetime of 1162, 1376, and 1464 μs, respectively. Some of the reported lifetime values for the ⁵D₀ level of Eu³⁺ in YVO₄ systems are 460–740 μs. And for direct excitation at 395 nm, the monoexponential equation: \( I = I₀ \ e^{−t/τ} \) is used to fit the decay profiles shown in Figure 6d and their lifetimes are given in Table 2. The average lifetimes for the as-prepared, 500 and 850 °C annealed samples are, respectively, 951, 1256, and 1278 μs. This indicates decrease in non-radiative transition probabilities owing to increased crystallinity on annealing and removal of defects/quenchers. The lifetimes are longer for excitation at 320 nm compared to the direct excitation at 395 nm. This is due to strong energy transfer from the host to the activator.

The decay profiles of the as-prepared YVO₄:5Eu³⁺, xLi⁺ (x = 0–15 at. %) and 500 °C-annealed YVO₄:5Eu³⁺, xLi⁺ samples for the excitation at 320 and 395 nm are presented, respectively, in Figures S5 and S6 (Supporting Information). Generally, for both the excitation wavelengths used, the lifetimes of the samples increase up to 5 at.% Li⁺ codoping. The lifetimes again decrease at 7 at.% Li⁺ codoping and then increase toward 15 at.% Li⁺ codoping. Their lifetime values are summarized in Table 2. Here, the lifetime values exhibit an increasing trend from 7 to 15 at.% Li⁺ codoping, but their emission intensities exhibit a decreasing trend. It is to be noted that, in the XRD pattern, the crystallinity increases as Li⁺ codoping increases. And the TEM images also revealed the favorable increase of particle size and enhanced crystallinity with Li⁺ doping. The increased crystallinity can have a positive influence on the efficiency of luminescence emission. The lifetime values also suggest increased population of the excited state of Eu³⁺ in the 7–15 at.% Li⁺-codoped samples. But the lifetime values are lower than the 5 at.% Li⁺-codoped sample. This could be the result of the relative position of Eu³⁺ in the nanocrystals with the increase of the particle size. There is also another possible speculated reason. The Li⁺ ion has 1s²2s⁰ configuration, that is, the 2s orbital is completely vacant. As the Li⁺ concentration increases, the proximity of Li⁺ to Eu³⁺ may increase. The hole in the Li⁺ ion in close proximity to Eu³⁺ or in the Eu³⁺–Li⁺ pair may serve as a non-radiative trap to quench the luminescence of Eu³⁺ even though the population of the electrons excited may increase. As a result of these factors, the luminescence intensities of Eu³⁺ fall as the concentration of Li⁺ increases beyond 5 at.% codoping. The speculative reasoning may require further experimental studies.

**CIE Coordinates, Dispersion-In-Water and Flexible Polymer Film Formation.** The color tone of the emitted light can be understood by examining the CIE color coordinates. The CIE coordinates are obtained by using the

Table 2. Lifetime Values of the Decay of the ⁵D₀ Level of Eu³⁺ Obtained after Fitting by the Equation: \( I = I₀ \ e^{−t/τ} \) for 320 nm Excitation and \( I = I₀ \ e^{−t/τ} \) for 395 nm Excitation

| sample                  | \( λ_{exc} = 320 \text{ nm} \) | \( \tau (\mu s) \) | \( R^2 \) | \( λ_{exc} = 395 \text{ nm} \) | \( \tau (\mu s) \) | \( R^2 \) |
|-------------------------|-------------------------------|-----------------|--------|-------------------------------|-----------------|--------|
| YVO₄:5Eu³⁺              | as-prepared                   | 710             | 0.99699| 658                           | 0.99378         |
| YVO₄:5Eu³⁺,1Li⁺         |                               | 678             | 0.99926| 725                           | 0.99870         |
| YVO₄:5Eu³⁺,3Li⁺         |                               | 930             | 0.99980| 923                           | 0.99948         |
| YVO₄:5Eu³⁺,5Li⁺         | as-prepared                   | 1162            | 0.99983| 951                           | 0.99888         |
|                        | 500 °C annealed               | 1376            | 0.99996| 1256                          | 0.99968         |
|                        | 850 °C annealed               | 1464            | 0.99995| 1278                          | 0.99944         |
| YVO₄:5Eu³⁺,7Li⁺         | as-prepared                   | 905             | 0.99980| 915                           | 0.99919         |
| YVO₄:5Eu³⁺,10Li⁺        |                               | 964             | 0.99955| 925                           | 0.99896         |
| YVO₄:5Eu³⁺,15Li⁺        |                               | 1054            | 0.99985| 1022                          | 0.99933         |

Here, \( λ_{exc} \) refers to the excitation wavelength.

Figure 7. (Left) CIE coordinates of the as-prepared (green dot), 500 °C (blue dot) and 850 °C (black dot) annealed YVO₄:5Eu³⁺, xLi⁺ samples. (Right) Emission spectra of the flexible polymer film (red line) and the dispersion in water (green line). Inset: Digital photographs of the polymer film formation.
CIE color matching function calculator for the color wavelength data ranging from 400 to 700 nm and the normalizing constant $K = 1$. The obtained coordinate values are $(0.58, 0.29)$, $(0.59, 0.29)$, $(0.58, 0.30)$, $(0.61, 0.33)$, $(0.60, 0.29)$, $(0.58, 0.29)$, and $(0.57, 0.30)$, respectively, for 0, 1, 3, 5, 7, 10, and 15 at. % Li$^+$ codoping. Whereas, those of the 500 and 850 °C annealed are, respectively, $(0.59, 0.33)$ and $(0.62, 0.33)$. The diagram showing the CIE coordinates of the as-prepared and annealed YVO$_4$:5Eu$^{3+}$,5Li$^+$ is shown in Figure 7 (left). It is therefore obvious that the samples exhibited a red emission.

In order to examine the possibilities of the samples for flexible display devices and bioimaging applications, the luminescence properties of the PVDF polymer film and dispersion-in-water of the YVO$_4$:5Eu$^{3+}$,5Li$^+$ sample are studied. Both the film and the dispersion are excited at 320 nm to determine their emission properties. The preparation of the flexible polymer film has been explained in the Experimental Section. For dispersion-in-water studies, 0.5–100 μg of the sample per mL of water is dispersed. Here, a stepwise dilution method is taken up to lower the concentration of dispersion. The representative emission spectra of the film and the dispersion-in-water are presented in Figure 7 (right). The digital photographs in the insets show the flexible polymer film and the red luminescence from the dispersion-in-water. As low as up to 0.5 μg dispersion gives a detectable/visible red emission. The emission spectra of the different concentrations of the dispersion-in-water are presented in Figure 8. The intensity of emission is observed to decrease linearly with concentration of nanocrystals. This may suggest that the concentration quenching effect in nanocrystals is an intrinsic effect dependent on the concentration of the activator in the nanocrystals but independent of the concentration of the nanocrystals in such a dispersion system. In addition, the dispersion-in-water is also subjected to different concentrations of H$_2$O$_2$ solution. The emission spectra of the YVO$_4$:5Eu$^{3+}$,5Li$^+$ sample dispersed in H$_2$O$_2$ solution are presented in Figure 9a. Their luminescence is not affected by the presence of H$_2$O$_2$ which implies that the material is not chemically disturbed by the oxidizing media.

In the previous literatures, YVO$_4$:Eu$^{3+}$ and EuVO$_4$ nanoparticles are reported as potential candidates for H$_2$O$_2$ sensing. The sizes of the particle that have efficient sensing were in the range of 20–40 nm. Some of the other key factors that affect the response toward the oxidant H$_2$O$_2$ are the defects, morphology, and crystallinity of the nanoparticle systems. In our case the YVO$_4$:Eu$^{3+}$,Li$^+$ nanoparticles have an average size of 200 nm along a dimension and appears to be an assembly of rodlike structures. The presence of Li$^+$ may have imparted different defect properties compared to YVO$_4$:Eu$^{3+}$ and EuVO$_4$. In addition, there is a big difference in the morphology and crystallinity of the nanoparticles as well as the presence of organic (glycerol) molecule adsorbed on the surface. Thus, it is highly possible that the larger size and low defects could be the reason for less sensitivity of the YVO$_4$:Eu$^{3+}$,Li$^+$ nanoparticles towards the oxidizing H$_2$O$_2$ media. Further, to study the robustness of the polymer film under an oxidative environment, it is treated with H$_2$O$_2$ solution and their luminescence is studied. Three films of (1 cm × 1 cm) are soaked separately in H$_2$O$_2$ solutions of three different concentrations for 1 h. After this, they were removed and kept at room temperature for a few minutes. The emission spectra are presented in Figure 9b. It was observed that the films are not wetted and their luminescence
CONCLUSIONS

Single phase YVO₄:Eu³⁺ₜₕ, Li⁺ nanocrystals with an enhanced red emission have been synthesized successfully. The optimum concentration is found to be 5 at. % for Li⁺ codoping. Further, annealing of the YVO₄:Eu³⁺ₜₕ, Li⁺ nanocrystals at 500 and 850 °C enhanced the crystallinity, luminescence emission, and the lifetime of Eu³⁺ emission. The heat treatment also improved the luminescence emission from the ⁵D₀ (J > 0) levels of Eu³⁺ as well as the lifetime of the ⁴D₀ level of Eu³⁺, which has been attributed to increased crystallinity. The lifetimes of the ⁴D₀ level of Eu³⁺ for YVO₄:SEu³⁺ and YVO₄:SEu³⁺ₜₕ, Li⁺ are, respectively, 710 and 1162 μs at 320 nm excitation. However, for direct excitation at 395 nm, the lifetimes of the ⁴D₀ level of Eu³⁺ for the YVO₄:SEu³⁺ and YVO₄:SEu³⁺ₜₕ, Li⁺ are 657 and 951 μs, respectively. The longer lifetime of the sample upon excitation at 320 nm implies an efficient energy transfer from VO₃³⁻ to Eu³⁺. The samples are readily dispersible in deionized water and show bright red luminescence at as low as 50 μg/mL. The decrease of the emission intensity linearly with the concentration of nanocrystals, may suggest that the concentration quenching effect in the nanocrystals is an intrinsic effect dependent on the concentration of the activator in the nanocrystals but independent of the concentration of the nanocrystals in such a dispersion system. The nanocrystals can also be readily incorporated into a flexible polymer film. The red emission from the dispersion-in-water and the polymer film are strongly resistant to the oxidizing H₂O₂ media. The resistance to oxidizing H₂O₂ may also be ascribed to the large size and decreased defects. Further analysis such as the use of a strong laser excitation source or cathodoluminescence may provide a clear insight into the luminescence behavior of the nanocrystals. And the factors affecting the luminescence such as the crystallite size and the lattice expansion may be clearly understood. Therefore, YVO₄:SEu³⁺ₜₕ, Li⁺ nanocrystals may be a promising luminescent material with a high luminescence yield and high chemical stability.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01265.

XRD patterns of the annealed samples; TEM images of YVO₄:SEu³⁺ and annealed YVO₄:SEu³⁺ₜₕ, Li⁺; emission spectra of the 500 °C annealed YVO₄:SEu³⁺ₜₕ, Li⁺; and luminescence decay profiles of the samples (PDF)

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ACKNOWLEDGMENTS

G.S.N. acknowledges the University Grants Commission for providing the Senior Research Fellowship. The authors are also grateful to Sophisticated Analytical Instrument Facility (SAIF), North Eastern Hill University (NEHU), Shillong for the TEM facility and the Department of Physics, Manipur University for the XRD facility.

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