Biphasic Sol–Gel Synthesis of Microstructured/Nanostructured YVO₄:Eu³⁺ Materials and Their H₂O₂ Sensing Ability

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ABSTRACT: Microstructured/nanostructured YVO₄:Eu³⁺ powders and films were synthesized through a biphasic sol–gel method, aiming at their application as H₂O₂ sensing materials based on the turn-off luminescence of Eu³⁺ ions. The synthesis was typically carried out at temperatures of 80 °C or lower by using organic solutions to dissolve vanadium alkoxide and aqueous solutions to dissolve yttrium and europium salts together with sodium carboxylates. The resultant crystalline YVO₄:Eu³⁺ powders and films were characterized as containing micrometer-sized particles comprising primary nanoparticles with high specific surface areas. A comparative study was performed on the H₂O₂-responsive turn-off luminescence properties for the above samples and those synthesized by a single-phase sol–gel or a conventional solid-state reaction method. The results indicated that the microstructural feature of the samples from the biphasic sol–gel method was effective for detecting H₂O₂ through its adsorption on the particle surface and quenching of the Eu³⁺ luminescence. The film samples showed repeatable and quantitative turn-off luminescence, thereby demonstrating their suitability as solid-state H₂O₂ sensors.

1. INTRODUCTION

Fluorescence can be used for detecting certain kinds of chemical species. This is based on changes of the fluorescence intensity or wavelength caused by the interaction between target chemical species and fluorescent materials. Much effort has been devoted so far to designing fluorescent materials aiming at biosensing and bioimaging. Besides traditional organic fluorescent dyes, quantum dots (QDs) have been intensively studied due to their higher stability and tunable fluorescence properties. They include semiconductor QDs such as CdS and CdSe, carbon dots, graphene QDs, and so on. There have also been inorganic phosphors that can be used as solid-state luminescence sensors. Due to their higher mechanical strength, thermal stability, and chemical durability, inorganic phosphors are suitable for application under severe circumstances such as high mechanical loads, high temperatures, or highly reactive conditions.

A key technique for realizing solid-state luminescence sensors is the precise control of the microstructure of inorganic phosphors in accordance with the respective sensing principles: dense bulks for stress sensing, thin films for high-temperature sensing, and nanoparticles for chemical sensing. In our previous studies, we focused on the luminescence sensing of redox species using rare-earth-activated phosphors (CePO₄:Tb⁵⁺, CeO₂:Sm³⁺, and CaWO₄:Eu³⁺) synthesized as nanorods, porous microspheres, or nanostructured films. In the present study, motivated by the increasing demand for the detection of hydrogen peroxide (H₂O₂), we attempted to synthesize microstructure-controlled YVO₄:Eu³⁺ phosphors. Among Eu³⁺-activated, red-emitting phosphors, YVO₄:Eu³⁺ is known to show highly efficient emissions because of the presence of the strongly light-absorbing VO₄⁻⁻ units that can easily transfer excitation energy to the doped Eu³⁺ ions. The highly efficient phosphors are favorable for designing sensors like turn-off type fluorescent probes. A difficulty arises, however, when applying the highly efficient phosphors to chemical sensors; they need to be synthesized as nanometer-scale particles having large surface areas. Generally, nanometer-scale phosphors are inferior to their bulk counterparts due to the much increased amount of surface defects that quench the luminescence considerably.

This is the specific reason for the necessity of the precise microstructural control of inorganic phosphors for chemical sensing applications.

We report herein our strategy and results for synthesizing micro-/nano-structured YVO₄:Eu³⁺ materials for H₂O₂ sensing. Contrary to the previous methods for the synthesis of YVO₄:Eu³⁺ nanomaterials, a biphasic sol–gel method has been employed because it is beneficial to obtaining microstructure-controlled materials ranging from nano- to micro-meter scales. This method is characterized by immiscible organic–aqueous solutions maintained still at low temperatures in a reaction container. Metal (M) alkoxides and metal (M⁺) salts are initially dissolved in organic and aqueous solutions, respectively. The alkoxides are hydrolyzed gradually (not vigorously) at the organic–aqueous interface. The

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resultant metal (M) hydroxide species move toward the aqueous phase where they meet the other metal (M’) ions to form compounds containing M and M’. Vanadium oxytriethoxide (VO(OC2H5)3) and yttrium/europium chloride (Y/Eu = 0.95:0.05 in mol) were used in the present study to precipitate YVO4:Eu3+ powders or deposit YVO4:Eu3+ films in the aqueous phase. Both the powders and the films had a specific microstructure characterized by their large surface areas, large pore volumes, and high crystallinity. Accordingly, we could evaluate them as H2O2-sensing materials with turn-off luminescence of the Eu3+ ions doped in the YVO4 host. The YVO4:Eu3+ films exhibited quantitative turn-off luminescence against the H2O2 concentration in aqueous solutions.

2. RESULTS AND DISCUSSION

2.1. YVO4:Eu3+ Powders. A comparative study was first performed for the synthesis of YVO4:Eu3+ powder samples by the sol–gel method with the above-mentioned biphasic system and a simple single-phase liquid system. A powder precipitated in the biphasic system (named BP) was initially tinged with yellow, as shown in Figure 1. The BP powder was then washed with a 1.0 M aqueous NaOH solution under stirring for 5 h as a base treatment. The color of the resultant powder (BP-BT) was changed to white during washing. Although the yellow color was lighter for a powder precipitated in the single-phase system (SP), the same base treatment was conducted to obtain SP-BT powder (Figure 1).

Figure 2 shows the X-ray diffraction (XRD) patterns of the BP, BP-BT, SP, and SP-BT powder samples. All the peaks appearing in the patterns can be indexed to the tetragonal YVO4 phase (ICDD 17-0341). Comparing their peak intensity, the powders obtained from the biphasic system exhibit higher intensities and are crystallized better than those obtained from the single-phase system. The crystallite size along the a-axis of the (200) peak using Scherrer’s equation.

X-ray fluorescence (XRF) analysis was carried out to examine the origin of the yellow color of the as-precipitated BP and SP samples. The V/(Y + Eu) ratio was determined to be 2.18 and 1.58 for BT and ST, respectively. This result indicates that the BP and SP samples have excess amounts of vanadium against a stoichiometric V/(Y + Eu) ratio of 1. Because of the lack of any XRD peaks due to a secondary phase in Figure 2, the excess vanadium is thought to be present in the samples as a vanadium oxide gel. On the other hand, the base-treated samples, BP-BT and SP-BT, had V/(Y + Eu) ratios of 1.16 and 1.06, respectively. The color of the BP-BT and SP-BT samples was also changed to white by the base treatment (Figure 1). The yellow colorization is therefore because of the vanadium oxide gel, which can be removed by washing in an aqueous NaOH solution. A further experiment was carried out to confirm the presence of the vanadium oxide gel before the base treatment. That is, the sample BP was annealed at 800 °C for 4 h in air in expectation of the crystallization of the amorphous gel. Figure S1 (see Supporting Information) shows a field-emission transmission electron microscopy (FETEM) image and a selected area electron diffraction (SAED) pattern of BP after annealing. The SAED pattern can be indexed to the orthorhombic V2O5 phase (ICDD 41-1426). This confirms that the excess vanadium exists separately from the (Y,Eu)VO4 phase in the sample BP.

The precipitation of the vanadium oxide gel in the samples BP and SP can be explained as follows. As reported in the literature,27 a large variety of chemical species containing V5+ ions exist in aqueous solutions depending on their pH values as well as V5+ concentrations ([V5+]). Any species stable at the respective pH values is defined in the log[V5+] – pH diagram.27 Among these, V2O5 is the most stable phase at both a lower pH and a higher log [V5+]. We observed in the biphasic system that the pH value of the aqueous solution decreased from 4.5 before the reaction to 3.6 after the reaction for 24 h. This pH decrease is because of the progress of the hydrolysis of VO(OCH3)3 and the subsequent formation of (Y,Eu)VO4 through a series of chemical reactions as described below.

\[
\begin{align*}
\text{VO(OCH}_3\text{)}_3 + 3\text{H}_2\text{O} & \rightarrow \text{VO}_2(\text{OH})_2^{2-} + \text{H}^+ + 3\text{C}_2\text{H}_5\text{OH} \\
(1 - x)\text{Y}^{3+} + x\text{Eu}^{3+} + \text{VO}_2(\text{OH})_2^{-} & \rightarrow \text{Y}_{1-x}\text{Eu}_x\text{VO}_4 + 2\text{H}^+ 
\end{align*}
\]

This reaction occurs when VO(OCH3)3 in the organic phase comes into contact with water molecules at the interface of the biphasic system. According to the diagram, VO2(OH)2– is stable at a low log [V5+] around pH = 4.5 and, therefore, H+ is released through the hydrolysis.

Then, the VO2(OH)2– ions react with Y3+ and Eu3+ in the aqueous phase to form Y1–Eu3VO4. This reaction also releases H+ and the pH value would be decreased further. However,
HOOO⁻ derived from HCOONa, which was added to the aqueous phase, works as a base and consumes H⁺ to achieve the following equilibrium reaction.

HCOO⁻ + H⁺ ⇌ HCOOH

(3)

Thus, the pH value steadies down to 3.6 after the 24 h reaction. With the progress of reactions 1 and 2, the stable V⁵⁺ species changes from VO₂(OH)₂⁻ to less-soluble V₂O₅, which has a great tendency to form an amorphous gel.²⁸

Figure 3 shows the photoluminescence (PL) excitation and emission spectra of the samples BP, BP-BT, SP, and SP-BT.

![Figure 3. PL excitation and emission spectra of the four YVO₄:Eu³⁺ powder samples (BP, BP-BT, SP, and SP-BT): an emission wavelength (λₑ) of 619.5 nm and an excitation wavelength (λₐx) of 280 nm were used for measuring the excitation and the emission spectra, respectively.](image)

Several sharp peaks are observed in both the excitation and the emission spectra. They are characteristic of the 4f–4f electronic transitions of Eu³⁺ doped in the YVO₄ phase,²⁹ thereby confirming that reaction 2 involves Eu³⁺ as the reactant in the present liquid-phase synthesis. Strong, broad excitation bands ranging from 220 to 360 nm are also seen in the PL excitation spectra of all the samples. They are assigned to the overlapping VO₄³⁻ absorption and O²⁻ → Eu³⁺ charge transfer (CT).³⁰,³¹

Because of the presence of the amorphous V₂O₅ gel, the PL intensity of BP and SP is much lower than that of BP-BT and SP-BT, respectively. According to the literature,³² the V₂O₅ gel has two absorption bands centered at 270 and 380 nm. The latter band is the reason for the yellow colorization and would have less influence on the Eu³⁺ emissions. In contrast, the former band overlaps with the CT band and a large part of the excitation light is absorbed by the V₂O₅ gel in the samples BP and SP. Therefore, the base treatment of these samples in the 1.0 M aqueous NaOH solution under stirring for 5 h effectively removes the V₂O₅ gel and enhances the Eu³⁺ emissions, as seen for the samples BP-BT and SP-BT in Figure 3.

It is also obvious in Figure 3 that the samples from the biphasic system exhibit a higher PL intensity than those from the single-phase system both before and after the base treatment. This is one of the major reasons why we employ the biphasic sol–gel method to produce phosphor materials. Formerly, we synthesized two kinds of self-activated luminescent materials, namely CaNb₂O₆ and Ba₂V₂O₇, by a similar biphasic method.³⁵,³⁶ In the case of CaNb₂O₆, particles obtained from the biphasic method had a rough and dimpled surface which was more suitable for the extraction of the emitted light. Ba₂V₂O₇ from the biphasic method also had better crystallinity and morphology for emission. A fundamental difference between the biphasic and the single-phase system lies in the reaction rate and the morphological evolution. The hydrolysis of the metal alkoxides proceeds much more slowly and mildly due to a very limited reaction space as well as a low amount of water at the organic–aqueous interface. The nucleation and crystal growth of Y₁−xEuₓVO₄, according to reaction 2, take much more time in the biphasic system and the precipitates are matured well. This is why the crystallinity is better (Figure 2) and hence the PL intensity is higher (Figure 3) for the samples from the biphasic system.

The photostability of the samples BP and BP-BT was evaluated because the nano-sized phosphors synthesized from the chemical solutions containing organic ligands often suffer from degradation during irradiation with the excitation light.³³,³⁴ Figure S2 shows the PL intensity at 619.5 nm plotted against time of the ultraviolet (UV) irradiation at 320 nm for the samples BP and BP-BT. While the PL intensity of BP, normalized to its initial intensity, decreases rapidly to 0.24 within 10 min, BP-BT maintains its intensity as high as 0.85 after 10 min. We confirmed from the Fourier-transform infrared (FT-IR) spectroscopy analysis that the HCOO⁻ ions were present in the sample BP and initially questioned whether they acted as the luminescence quencher. However, we came to know later that a film sample also had low photostability even after annealing at 400 °C for 3 h in air: the photostability was finally improved after the base treatment. Because the HCOO⁻ ions were no longer present in the annealed film, we consider that the low photostability of the sample BP arises from the amorphous V₂O₅ gel.

Figure 4a shows the field-emission scanning electron microscopy (FESEM) images of the samples BP-BT and SP-

![Figure 4. (a) FESEM and (b) FETEM images of the YVO₄:Eu³⁺ powders after the base treatment (BP-BT and SP-BT).](image)
primary nanoparticles than the sample SP-BT, indicating that the crystal growth was promoted in the biphasic system. This result also supports the higher PL intensity of the BP-BT sample as mentioned above.

Figure 5 shows the N₂ adsorption–desorption isotherms and pore size distribution curves of BP-BT and SP-BT. The isotherm of both BP-BT and SP-BT corresponds to that of type IV with a type H2 hysteresis loop in the IUPAC classification. This suggests that the present YVO₄:Eu³⁺ particles have mesopores with an ink bottle shape. The fitting analysis based on the Brunauer–Emmett–Teller (BET) equation revealed that the specific surface areas of BP-BT and SP-BT were 157 and 67.4 m² g⁻¹, respectively. The pore size distribution was examined using the MP and the Barrett–Joyner–Halenda (BJH) method. It is seen from Figure 5b,c that both BP-BT and SP-BT have micropores and mesopores with diameter ranges of 0.7–2 and 2–10 nm, respectively. The pore volume is larger in BP-BT than in SP-BT. These results demonstrate that the micro-/nano-structured particles from the biphasic system are promising as porous sensing materials.

To examine the H₂O₂-sensing ability of our YVO₄:Eu³⁺ micro-/nano-structured particles, PL spectra were measured before and after immersing them in a 100 ppm H₂O₂ solution. As shown in Figure S3, there seems to be no systematic trend between the PL intensity and the amount of the powders. Note that the sample SS was composed of micrometer-sized particles and its specific surface area was as low as 0.8 m² g⁻¹. It is seen from Figure 6 that BP-BT and SP-BT undergo a decrease of 33 and 18%, respectively, in their PL intensity after immersion in the 100 ppm H₂O₂ solution. This observation indicates that the micro-/nano-structured particles from the biphasic system have higher H₂O₂-sensing ability based on the PL quenching because of their higher specific surface areas and larger pore volumes.

Figure 5. (a) Adsorption–desorption isotherm plots for nitrogen sorption at 77 K, and (b) BJH and (c) MP pore size distribution curves of the BP-BT and SP-BT samples.

Figure 6. PL excitation and emission spectra of the YVO₄:Eu³⁺ powders of (a) BP-BT, (b) SP-BT, and (c) SS before and after immersing in a 100 ppm aqueous H₂O₂ solution.
2.2. YVO₄:Eu³⁺ Films. For the possible sensing applications, it is favorable that the micro-/nano-structured particles are fixed on substrates to facilitate their handling. Films of YVO₄:Eu³⁺ were then deposited on silica glass substrates from the biphasic system with the addition of HCOONa (film F) or CH₃COONa (film A) in the aqueous phase. Figure 7 shows XRD patterns of the films F and A after annealing at 400 °C for 3 h and base treatment for 1 h. All the peaks appearing in the patterns can be indexed to the tetragonal YVO₄ phase (ICDD 17-0341). The pattern of film A exhibits a prominent (200) peak as compared to the other weakened peaks, thereby indicative of a preferential a-axis orientation of the particles grown on the substrate.

Figure 8 shows FESEM and FETEM images of the films F and A. From the surface FESEM images at low magnification, both film F and A consist of micrometer-sized spherical particles. These particles originate from the initial heterogeneous nucleation at the substrate surface, the subsequent homogeneous nucleation in the aqueous phase, and the final growth together on the substrate. The size of the spherical particles is observed to be 1.0–4.0 and 1.0–2.0 μm for film F and A, respectively. As a whole, the spherical particles of film A are smaller than those of film F, and the accumulation of the particles is denser in film A than in film F. From the surface FESEM images at high magnification in Figure 8a and FETEM images in Figure 8b, it can be seen that the micrometer-sized spherical particles are actually constructed of primary nanoparticles, similar to the YVO₄:Eu³⁺ powder obtained from the biphasic system. The primary nanoparticles in film F are spherical in shape, whereas those in film A have a sheet-like structure. From the cross-sectional FESEM images, the thickness of film A is observed to be larger than that of film F. This difference would cause changes in the optical properties between the films. For example, the diffuse reflectance of film A in the visible light region is twice or many times as high as that of film F, as shown in Figure S4.

We found that film A was attached more tightly to the substrate than film F. This was confirmed experimentally through the repetition of immersing/heating treatments of the films as described below. As seen from Figure 8, the surface of the substrate is fully covered by the densely accumulated smaller particles in film A, whereas film F exhibits an uncovered substrate surface due to the inhomogeneous distribution of the particles. Such a difference may originate from the nucleation stage of the film deposition. An experiment was then performed to compare the number of the particles formed on the substrate through the initial heterogeneous nucleation. That is, the substrate was made to stand against the wall of a glass centrifuge tube when the films (called film F' and A' in this experiment) were deposited using the biphasic system under the same reaction conditions. Figure S5 shows the FESEM images of the substrate surface after the reaction. A clear difference is observed between film F' and A' in the number and the size of the particles formed on the substrate. The larger number and the smaller size of the particles in film A' coincide with those observed for film A. This is why the connection between the particles and the substrate, as well as that among the particles, is sufficiently strong in film A, which is important for its application as the H₂O₂ sensor.

The enhanced heterogeneous nucleation in film A can be explained as follows. HCOOH and CH₃COOH have pKₐ values of 3.75 and 4.76, respectively. Because the pH value of the aqueous phase before the reaction was measured to be 4.50, the concentrations of HCOO⁻ and CH₃COO⁻ can be calculated to be 0.085 and 0.024 M, respectively, according to the formula \(\text{pH} = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)\) (A = HCOO or CH₃COO). In the aqueous phase, the HCOO⁻ and the CH₃COO⁻ anions can react with the Y³⁺ (0.095 M) and the Eu³⁺ cations (0.005 M) to form complexes, which decreases the concentration of the free Y³⁺ and Eu³⁺ cations. Due to the higher HCOO⁻ concentration, reaction 2 is retarded and the formation of Y₁₋₂Eu₂VO₄ is suppressed in the deposition of film F. In contrast, the heterogeneous nucleation becomes
more frequent on the substrate in the case of film A because of the lower CH$_3$COO$^-$ concentration.

Figure 9 shows PL excitation and emission spectra of film F and A, those immersed in the 100 ppm aqueous H$_2$O$_2$ solution (film F-I and A-I), and those subsequently heated at 200 °C in air (film F-H and A-H). The scale of the vertical axis is the same for the two graphic charts (a,b).

(film F-I and A-I), and those subsequently heated at 200 °C in air (film F-H and A-H). Both film F and A exhibit a remarkable decrease in the PL intensity after immersing in the H$_2$O$_2$ solution (F-I and A-I). This H$_2$O$_2$ sensitivity corresponds with that observed for the powder sample (Figure 6). We confirmed here that the PL intensity did not change when the films were immersed in water. The decreased PL intensity of the H$_2$O$_2$-treated films is then recovered by heating in air at 200 °C (F-H and A-H).

The H$_2$O$_2$ sensitivity, as observed in the decreasing PL intensity, of the micro-/nano-structured YVO$_4$:Eu$^{3+}$ particles and films may have a different mechanism than that observed in our previous redox-responsive phosphor materials$^{7-11}$ If the PL quenching is because of the surface redox reaction between H$_2$O$_2$ and YVO$_4$:Eu$^{3+}$ to promote the V$^{5+}$ → V$^{4+}$ reduction, the PL intensity can possibly be recovered by the reverse redox reaction using oxidants. However, the PL intensity was not recovered by the typical oxidizing treatment of film F-I by immersing in a 100 ppm KMnO$_4$ aqueous solution for 10 min, as shown in Figure S6. This implies that the H$_2$O$_2$-treated film F-I had not been reduced and therefore the PL recovery would need different treatments.

The other plausible cause for the PL quenching is the photocatalytic activity of YVO$_2$:Eu$^{3+}$ for decomposing H$_2$O$_2$. It was reported that the YVO$_2$:Eu$^{3+}$ nanoparticles could decompose methyl orange under UV irradiation.$^{36}$ The photoexcited electrons and holes are consumed to decompose the H$_2$O$_2$ molecules that are adsorbed on the surface of the YVO$_4$:Eu$^{3+}$ particles. The energy transfer to the Eu$^{3+}$ ions is then disturbed and their emission intensity is diminished. We found this mechanism possible because the quenched PL in film F-I could be recovered by continuous irradiation with 300 nm UV light, as shown in Figure 10. An almost linear recovery of the PL intensity with the irradiation time corresponds to the progress of the decomposition of H$_2$O$_2$ and the increase in the energy transfer to the Eu$^{3+}$ ions. Without the adsorbed H$_2$O$_2$, YVO$_2$:Eu$^{3+}$ adversely shows a slight decrease in its PL intensity as seen for film F in Figure 10. The large surface areas as well as the highly porous structure of the particles would be beneficial for preserving the H$_2$O$_2$ molecules inside them during the immersion treatment.

Reproducible and repeatable H$_2$O$_2$-sensing ability should be achieved to fabricate a reliable sensor using the micro-/nano-structured YVO$_4$:Eu$^{3+}$ films. Figure 11a shows changes of the relative PL intensity (integrating emissions between 500 and 750 nm) of film A after repeating five cycles of the immersion in the 100 ppm aqueous H$_2$O$_2$ solution and the heating at 200 °C in air, and (b) diffuse reflectance spectra of film A and A-HS after five cycles of the immersion/heat treatment.
the five-cycle treatments are almost the same (Figure 11b); the particles constructing the film were not detached. In contrast, film F had a lower mechanical strength and was peeled off after the second heat treatment.

Finally, a quantitative H$_2$O$_2$-sensing ability was evaluated. Four kinds of film A-I were prepared by using aqueous H$_2$O$_2$ solutions of 25, 50, 75, and 100 ppm. The relative PL intensity (integrating emissions between 500 and 750 nm) of the films was normalized with that of film A taken as unity. Figure 12 shows a plot of the relative PL intensity against the H$_2$O$_2$ concentration. The intensity decreases linearly with the increasing H$_2$O$_2$ concentration, thereby indicating the excellent quantitativeness in H$_2$O$_2$ sensing. The linearity also supports the PL quenching mechanism, which basically depends on the amount of adsorbed H$_2$O$_2$ molecules, as discussed above.

3. CONCLUSIONS

The micro-/nano-structured YVO$_4$:Eu$^{3+}$ powders and films were synthesized and their H$_2$O$_2$ sensing ability was evaluated. The PL emission intensity of the Eu$^{3+}$ ions was decreased when the YVO$_4$:Eu$^{3+}$ samples were immersed in a 100 ppm aqueous H$_2$O$_2$ solution for 10 min at room temperature. The intensity could then be recovered by heating the samples at 200 °C for 10 min in air. The film sample showed repeatable PL quenching and recovery at least up to five cycles, and also quantitative PL quenching against the H$_2$O$_2$ concentration. The mechanism underlying the PL quenching was suggested to be the consumption of photogenerated electron–hole pairs by the decomposition of the H$_2$O$_2$ molecules adsorbed on the YVO$_4$:Eu$^{3+}$ samples. Our results demonstrate that the microstructure-controlled phosphor materials are promising as solid-state luminescence sensors for detecting chemical species by effective surface interaction.

4. EXPERIMENTAL SECTION

4.1. Liquid-Phase Synthesis of Powders. The biphasic sol–gel synthesis of the YVO$_4$:Eu$^{3+}$ powder was carried out as follows. A 1.00 mmol (187 μL) portion of VO(OC$_2$H$_5$)$_3$ (95.0%, Aldrich) was dissolved in 10.0 mL of ethanol (99.0%, Amakasu Chemical Industries). The resultant solution was then added to 90.0 mL of water without stirring, was washed with deionized water, and was dried at 60 °C for a few hours. The dried powder, tinged with yellow, was further washed with 1.0 M aqueous NaOH solution under stirring for 5 h as the base treatment. The color of the powder changed to white during the washing. Finally, the white powder (BP-BT) was collected again by suction filtration, washed with deionized water, and dried at 60 °C for a few hours.

For the comparative study, another powder was synthesized in the simple single-phase liquid system. The aqueous solution employed for this synthesis was the same as that used in the above biphasic system. A 7.0 mL aliquot of the aqueous solution was placed in a glass centrifuge tube. Then, 0.7 mL of the ethanolic VO(OC$_2$H$_5$)$_3$ solution, which had been used to prepare the organic solution, was poured directly into the aqueous solution. The resultant solution was kept at 80 °C for 24 h. The precipitate (SP) was collected by suction filtration, washed with deionized water, and dried at 60 °C for a few hours. The base treatment was also carried out in the same way as described above to obtain the SP-BT powder.

4.2. Solid-State Synthesis of Powder. As the reference sample, the stoichiometric YVO$_4$:Eu$^{3+}$ powder was synthesized by the conventional solid-state reaction method. Commercial powders of Y$_2$O$_3$ (99.99%, Wako), Eu$_2$O$_3$ (99.9%, Wako), and V$_2$O$_5$ (99.0%, Wako) were mixed in a molar ratio of Y/Eu/V = 0.95:0.05:1 using a pestle and mortar with the addition of acetone. The resultant mixture was dried at room temperature and then heated at 1200 °C for 6 h in air to obtain the YVO$_4$:Eu$^{3+}$ powder (SS).

4.3. Liquid-Phase Synthesis of Films. The substrates employed in the present study were silica glass plates, 12.6 mm × 12.6 mm in dimensions and 1 mm in thickness. The solutions used for film deposition were almost the same as those used for powder synthesis in the biphasic system. Additionally, 3.00 mmol of CH$_3$COONa (98.5%, Wako) was also selected as the additive, instead of 4.50 mmol of HCOONa, in attempting to modify the nucleation process during the film deposition. The substrate was placed horizontally at the bottom of the glass centrifuge tube so that the film can be deposited on its upper side. A 7.0 mL aliquot of the aqueous solution containing HCOONa or CH$_3$COONa was added to the tube so that the substrate could be immersed completely. A 7.0 mL aliquot of the organic VO(OC$_2$H$_5$)$_3$ solution was then poured into the tube to prepare the biphasic system. The system was kept at 50 °C for 24 h to promote the film deposition. Subsequently, the substrate was removed from the tube, followed by washing with deionized water and drying at room temperature. The film thus obtained on the substrate was annealed at 400 °C for 3 h in air. The annealed film underwent the base treatment for 1 h without stirring, was washed with deionized water, and was finally dried at room temperature.

4.4. H$_2$O$_2$ Treatment of Powders and Films. 9.0 μL of a 30 wt % aqueous H$_2$O$_2$ solution (Wako) was added to 30 mL of deionized water to prepare the 100 ppm H$_2$O$_2$ solution. The
pH value of the H₂O₂ solution was measured to be 5.8–6.1, which was almost the same as that of deionized water. The powder samples (30 mg of BP-BT, SP-BT, or SS) were added to the resultant H₂O₂ solution and kept at room temperature for 10 min under stirring. The powders were collected by suction filtration, washed with deionized water, and dried at 60 °C for a few hours. The turn-off luminescence of the powders was examined by measuring the emission spectra before and after the H₂O₂ treatment.

Separately, the relationship between the turn-off luminescence and the amount of the powder was investigated for the samples obtained from the biphasic system. The BP-BT powder samples, with their amounts varied between 3.4 and 47.3 mg, were added to 10 mL of the 100 ppm H₂O₂ solution and kept at room temperature for a prolonged time (1 h) under stirring. The turn-off luminescence of the collected powders was then examined similarly.

The film samples were immersed in the 100 ppm H₂O₂ solution for 10 min at room temperature. The films were removed, washed with deionized water, and dried at room temperature. Additionally, the films were annealed at 200 °C for 10 min in air in order to desorb or decompose the H₂O₂ molecules. The PL of the films was examined similarly before and after the H₂O₂ treatment and also after annealing.

For the quantitative evaluation of the H₂O₂-sensing ability, four kinds of film A1–A4 were prepared by using aqueous H₂O₂ solutions of 25, 50, 75, and 100 ppm and their PL intensity was measured. The experiment was repeated four times for the respective film samples to deduce the standard deviation.

4.5. Characterization. The crystalline phases of the samples were identified by XRD analysis (D8 ADVANCE diffractometer, Bruker AXS) using Cu Kα radiation. The crystal size was calculated from the full width at half maximum of the XRD peak using Scherrer’s equation with a K value of 0.937. The microstructure of the samples was observed by FESEM (Inspect F50, FEI, or S-4700 microscope, Hitachi). The specimen for the FESEM observation was prepared by dispersing the powders in ethanol and drying on a carbon coated copper grid. The morphology of the samples was observed by FESEM (Inspect F50, FEI, or S-4700 microscope, Hitachi). Conductive coating was applied to the samples with an osmium plasma coater. The chemical composition of the powder samples was examined by XRF spectroscopy (XGT-2700 analytical microscope, Horiba). The stoichiometric Y₀.₉₅Eu₀.₀₅VO₄ powder synthesized by the solid-state reaction method was used as the reference. The pH value of the aqueous solution was measured at room temperature with a pH meter (model F-51, Horiba) and a pH electrode (model 961SS-10D, Horiba). The PL spectra and the photostability of the samples were measured at room temperature with a spectrophotofluorometer (model FP-6500, JASCO) using a xenon lamp (150 W) as the light source. The powder samples were mounted on a silica glass plate having a square well 5 mm × 5 mm in dimensions to regulate their amount in the PL measurement. The film samples were measured when they were mounted directly on the attachment. The diffuse reflectance spectra of the film samples were measured with a UV-visible spectrophotometer (model V-670, JASCO) in the wavelength range between 200 and 800 nm. An integrating sphere (model ISN-723, JASCO) was used together with a Spectralon diffuse reflectance material. The BET surface area and the pore size distribution of the powder samples were evaluated by using nitrogen adsorption–desorption apparatus (model BELSORP-mini II, MicrotracBEL). The presence of organic species in the samples was examined by FT-IR (ALPHA spectrometer, Bruker Optics).

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02915.

The TEM analysis of the annealed powder sample (Figure S1), the photostability of the powder samples (Figure S2), the dependence of the H₂O₂ sensitivity on the amount of the powder samples (Figure S3), the optical properties of the films (Figure S4), the films on the substrate which was made to stand against the wall (Figure S5), and the oxidizing treatment with KMnO₄ (Figure S6) (PDF)

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Notes
The authors declare no competing financial interest.

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