Ultra-Weak Chemiluminescence Enhanced by Cerium-Doped LaF$_3$ Nanoparticles: A Potential Nitrite Analysis Method

Yufei Wang $^1$, Yanran Wang $^1$, Chunxia Huang $^1$, Tianyou Chen $^1$ and Jing Wu $^{1,2,*}$

$^1$ School of Science, China University of Geosciences, Beijing, China, $^2$ Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, Qingdao University of Science and Technology, Qingdao, China

In this work, cerium-doped LaF$_3$ nanoparticles (LaF$_3$:Ce NPs) were successfully synthesized and characterized. Its chemiluminescence (CL) property was studied, and it was amazingly found that it intensely enhanced the ultra-weak CL of the NaNO$_2$-H$_2$O$_2$ system. The CL mechanism was systematically investigated and suggested to be the recombination of electron-injected and hole-injected LaF$_3$:Ce NPs. The new CL system was developed to be a facile, original, and direct method for nitrite analysis. Experimental conditions were optimized and then a satisfactory linear relationship between CL intensity and nitrite concentration was obtained. This work introduced a new pathway for the research and application of traditional fluoride NPs doped with RE$^{3+}$.

Keywords: chemiluminescence, cerium, fluoride, nitrite, nanoparticles

INTRODUCTION

Fluoride is utilized as an ideal and appealing host for phosphors doped with rare earth ions (RE$^{3+}$) owing to its adequate thermal and environmental stability as well as large solubility for RE$^{3+}$ ions (Li et al., 2012). Compared with oxide systems, vibrational energies in fluorides is low and therefore trigger scarce quenching of the excited states of the RE$^{3+}$ ions (Bender et al., 2000). Furthermore, RE$^{3+}$-doped fluorides exhibit characteristic properties, such as high ionicity, low refractive index, wide band gap, and low phonon energy. KMgF$_3$ (Schuyt and Williams, 2018), NaYF$_4$ (Wu et al., 2019, 2020), NaGdF$_4$ (Yi et al., 2019), and LaF$_3$ (Bekah et al., 2016; Nampoothiri et al., 2017) have been investigated and exhibit high quantum yields and long luminescent lifetimes. RE$^{3+}$-doped fluorides have been attracting attentions for several years due to the wide variety of technological applications including biomedical researches (All et al., 2019; Yan et al., 2019), biosensors (Vijayan et al., 2019), bioimaging (Hu et al., 2016; Han et al., 2017; Zeng et al., 2019), radiation detection (Ju et al., 2017), optoelectronic devices (Wu et al., 2018), and so on. However, to the best of our knowledge, the performance of RE$^{3+}$-doped fluorides toward chemiluminescence (CL) has not been explored.

Nitrite is widely used in food manufacture as preservatives and fertilizing reagents. As an essential precursor of carcinogenic N-nitrosamine, excess intake of nitrite is harmful for human beings. Nitrite can cause irreversible conversion of hemoglobin to methemoglobin in the bloodstream and then bring detrimental effect for the oxygen transport in the whole body. In addition, nitrogen-based fertilizers and industrial wastewater pollute groundwater resources by nitrates. Thus, nitrite detection is of significant importance for food safety, public health, and environment protection (Wang et al., 2017; Zhang Y. et al., 2018; Cao et al., 2019).
Various principle-based analytical methods have been devised for nitrite detection, such as electrochemical sensors (Ma et al., 2018; Wang et al., 2018; Zhou et al., 2019; Madhuvilakkal et al., 2020), microplasma emission (Zheng et al., 2018), absorption spectrophotometry (Zhang et al., 2018), fluorescence (Dai et al., 2017; Jana et al., 2019; Pires et al., 2019), and CL (Lu et al., 2002, 2004; Lin et al., 2011; Wu et al., 2016). Electrodes are modified with complex strategies in electrochemical analysis. Special molecules need to be designed for spectrophotometric detections in order to amplify signal and reduce the background interferences. CL detections require simple instruments, interfere with low background, and are compatible with gas or aqueous phases. CL intensity was reported to be significantly enhanced by nanomaterials that gave promise for developing sensitive and convenient CL analytical methods. In 2011, carbon dots were firstly demonstrated to enhance the CL signal of the NaNO2-H2O2 system because of peroxynitrous acid generation (Lin et al., 2011). Nitrogen-rich quantum dots (QDs) were facilely synthesized and intensely enhanced the ultra-weak CL reaction of the NaO2-H2O2 system through electron hole injection and CL resonance energy transfer (Zheng et al., 2017). In particular, molybdenum sulfide QDs were proved to give rise to the generation of reactive oxygen species from hydrogen peroxide (H2O2) in alkaline solution and gave a promise for CL emission (Dou et al., 2019). However, fluoride-based nanomaterials were scarcely utilized and the developed CL analysis was rarely applied in nitrite detection. Original CL detections for nitrites are worth giving research to pursue better performance.

In this work, cerium-doped LaF3 nanoparticles (LaF3:Ce NPs) were synthesized and firstly demonstrated to enhance the CL signal of the NaNO2-H2O2 system. Reactive oxygen species generation that was triggered by LaF3:Ce NPs was proved to be the main reason for CL enhancement. A linear relationship between the CL signal and nitrite concentration was found and implied that the LaF3:Ce NPs-NaNO2-H2O2 system could be applied in the determination of nitrite.

**MATERIALS AND METHODS**

**Reagents and Materials**

Sodium nitrite (NaNO2) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sulfuric acid (H2SO4, 98%), H2O2 (35%), hydrochloric acid, and ethanol (98%) were bought from Beijing Chemical Reagent Co. (Beijing, China). Sodium fluoride (NaF, >98%), heptahydrate lanthanum chloride (LaCl3·7H2O, 99.9%), heptahydrate cerium chloride (CeCl3·7H2O, 99.9%), oleic acid (90%), 5,5-dimethyl-1-pyrrrole N-oxide (DMPO), and ascorbic acid (AA) were all purchased from Sigma-Aldrich. Unless otherwise noted, all the chemicals were used without further purification.

**Apparatus**

UV-vis absorption spectra were performed on a PerkinElmer Lambda 950 spectrophotometer. The photoluminescent (PL) spectra were collected on an Agilent Cary Eclipse spectrofluorometer. Fourier transform infrared (FT-IR) spectra were obtained on a PerkinElmer Frontier FT-IR spectrometer. CL experiments were conducted with an ultra-weak CL analyzer (IFFM-E, Xi’an Remex Analytical Instrument Co., Ltd, China). Transmission electron microscopy images were obtained on a JEOL-1400 transmission electron microscopy machine (JEOL, Tokyo, Japan). Electron paramagnetic resonance (EPR) spectra were measured on a Bruker E500 spectrometer.

**LaF3:Ce NPs Synthesis**

Hydrothermal reaction was utilized to synthesize LaF3:Ce NPs. 2.25 ml of LaCl3 solution (0.20 M), 1.00 ml of CeCl3 solution (0.05 M), 2.00 ml of NaF solution (1.00 M), 20 ml of ethanol, and 10 ml of oleic acid were mixed and stirred for 0.5 h in reaction kettle. The mixture was heated in an oven and kept at 200°C for 8 h. After reaction, the supernatant was removed. The remnant suspension was centrifuged at 6,000 rpm for 5 min and then the supernatant was also removed. The resultant solid was dispersed in 2.00 M hydrochloric acid. After ethanol addition, the mixture was centrifuged at 6,000 rpm for 5 min to remove the supernatant. The product was stored in 4 ml H2O for further use. The exact doping percentage of cerium was calculated to be 10%.

**CL Study of the LaF3:Ce NPs-NaNO2-H2O2 System**

At first, CL intensities of the NaNO2-H2O2 system with and without LaF3:Ce NPs were compared. Fifty microliters of H2O2 (3.00 M), which was acidified by 0.04 M H2SO4, was injected into the mixture of 50 µl of LaF3:Ce NPs and 50 µl of NaNO2 (10 µM). In the control experiment, 50 µl of LaF3:Ce NPs was replaced by 50 µl of H2O. CL intensities of both the two conditions were recorded and compared. CL profiles were integrated at intervals of 0.1 s. Voltage of the photomultiplier tube (PMT) was set at 1.2 kV. CL spectrum was measured with high-energy cutoff filters (400–640 nm), which were set between the quartz cuvette and PMT as described in Cui et al. (2003). Additional orders of the reagents were investigated to collect CL kinetic curves. EPR measurements were operated at an X-band frequency of 9.85 GHz. Irradiation was performed by using a 300-W Xe lamp (300 nm < λ < 1,100 nm) with the output radiation focused on the samples in the cavity by an optical fiber (50 cm length, 0.3 cm diameter). All spectra were acquired at 298 K. DMPO (12.4 µM in 1 ml of H2O) was taken as the specific detection reagent for -OH. AA (0.1 mM) was used as a scavenger for O2·-. CL intensities of the LaF3:Ce NPs-NaNO2-H2O2 system with and without AA were recorded.

**Nitrite Analysis**

Experimental conditions were optimized with different H2SO4 concentrations (0, 0.02, 0.03, 0.04, 0.05, and 0.06 M), H2O2 concentrations (0.00, 1.00, 2.00, 3.00, 4.00, and 5.00 M), and additional volumes of LaF3:Ce NPs (0, 10, 20, 30, 40, 50, 60, and 70 µl). The univariate method was adopted in systematically
optimizing experimental parameters through changing one parameter at a time while keeping others constant. At the optimal experimental conditions, calibration curve was recorded by detecting CL intensities vs. different nitrite concentrations.

RESULTS

Characterization of LaF₃:Ce NPs
LaF₃:Ce NPs obtained in this work exhibited hexagonal phase and their average sizes were about 80 × 20 nm (Figure 1A). 4f shells of lanthanides are partially filled and are effectively shielded by outer 5s and 5p shells leading to satisfactory emissions. The prepared LaF₃:Ce NPs gave a bright blue color under ultraviolet radiation (λₑₓ = 254 nm) (Figure 1B, inset). The emission of LaF₃:Ce NPs shifted to longer wavelength with the increase of excitation wavelength revealing the distribution of different surface energy traps of the LaF₃:Ce NPs (Figure 1B). UV-vis absorption spectra of the LaF₃:Ce NPs-NaNO₂-H₂O₂ system were collected and are shown in Figure 1C. NaNO₂ gave an absorption peak at 354 nm, which decreased when acidified H₂O₂ was added. Another absorption peak located at 301 nm appeared due to the isomerization of ONOOH, which was generated in the mixture of acidified H₂O₂ and NaNO₂ (Lin et al., 2011), while no new absorption peaks were found when acidified H₂O₂ mixed with LaF₃:Ce NPs. Except the absorption peak of ONOOH, no other new absorption peak was found in the LaF₃:Ce NPs-NaNO₂-H₂O₂ system, indicating that no new compound was formed. UV-vis absorption spectra gave some indications for the CL mechanism of this system, which was illustrated in detail in the subsequent section. FT-IR spectrum of LaF₃:Ce NPs indicated that there were O-H groups on the surface of LaF₃:Ce NPs (Figure 1D).

CL of the LaF₃:Ce NPs-NaNO₂-H₂O₂ System
CL intensities of the NaNO₂-H₂O₂ system with and without LaF₃:Ce NPs were sharply different. LaF₃:Ce NPs addition intensely enhanced CL intensity (Figure 2A). As shown in Figure 2B, the CL spectrum for the LaF₃:Ce NPs-NaNO₂-H₂O₂ system was wide ranging from 375 to 500 nm and was centered

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**FIGURE 1** Characterization of LaF₃:Ce NPs. (A) Transmission electron microscopy images of LaF₃:Ce NPs. (B) PL spectra of LaF₃:Ce NPs. The inset is the photograph of LaF₃:Ce NPs under a UV lamp (λₑₓ = 254 nm). (C) UV-vis absorption spectra of the reagent in the CL reaction. (D) FT-IR spectra of LaF₃:Ce NPs.
at 450 nm. The fluorescent emission of LaF$_3$:Ce NPs is also wide, which is similar to the CL spectrum of the LaF$_3$:Ce NPs- NaNO$_2$- H$_2$O$_2$ system. As a result, it is reasonable to refer that the CL originates from the various surface energy traps existing on the LaF$_3$:Ce NPs. Compared with the PL peak of LaF$_3$: Ce NPs, the CL spectrum is red-shifted due to the energy separations of LaF$_3$:Ce NPs surface states. PL was generated through excitation and emission within the core of the LaF$_3$:Ce NPs and the energy gap between them is larger than the energy separations on NPs surface (Ding et al., 2002; Myung et al., 2002).

**CL Kinetic Study**

As described in UV-vis absorption spectra, ONOOH was generated when NaNO$_2$ was mixed with acidified H$_2$O$_2$ (Equation 1) (Anbar and Taube, 1954). ONOOH easily transforms to be nitrate via the stage of HOONO$^*$ and give emissions during the process (Equation 2) (Houk et al., 1996). The emission locates at 350–450 nm, which overlaps the absorption spectrum of LaF$_3$:Ce NPs. Hence, LaF$_3$:Ce NPs can be excited by the energy of transformation and cause CL emission. However, the maximum of the transformation-derived CL was obtained at the pH value of 6.5–7.0 while the maximum CL of the LaF$_3$:Ce NPs-NaNO$_2$- H$_2$O$_2$ system was recorded in a severe acidic solution (Starodubtseva et al., 1999). As a consequence, the transformation energy only partially contributed to the CL of the LaF$_3$:Ce NPs-NaNO$_2$- H$_2$O$_2$ system. Various mixing orders of reagents influenced the reactions between LaF$_3$:Ce NPs and ONOOH and then affected the CL intensities (Figure 3A). The highest CL was obtained when acidified H$_2$O$_2$ was injected into the mixture of LaF$_3$:Ce NPs and NaNO$_2$. At this condition, the generated ONOOH adequately reacted with LaF$_3$:Ce NPs and gave enhanced CL. Mixing of NaNO$_2$ with acidified H$_2$O$_2$ without LaF$_3$:Ce NPs gave weak and lasting CL while mixing of LaF$_3$:Ce NPs with acidified H$_2$O$_2$ without NaNO$_2$ gave weak and rapid CL (Figure 3B).

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\text{HNO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{ONOOH} + \text{H}_2\text{O} \quad (1)
\]
\[
\text{ONOOH} \rightarrow \text{ONOOH}^* \rightarrow \text{NO}_3^- + \text{H}^+ \quad (2)
\]

**CL Mechanism**

According to the CL kinetic study, it demonstrated that the reactions between LaF$_3$:Ce NPs and ONOOH or its related species were the main cause accounting for the enhanced CL. ONOOH was reported to be capable of producing reactive oxygen species (Equations 3–5) (Alvarez et al., 1995; Gunaydin and Houk, 2008; Lin et al., 2011). It was obvious that ONOOH-produced reactive oxygen species include ·OH, O$_3^-$, and $^1$O$_2$ in this system. EPR was performed and DMPO was utilized as the specific detection reagent for ·OH to directly examine the variation of ·OH after LaF$_3$:Ce NPs addition. Although CL intensity of the LaF$_3$:Ce NPs-NaNO$_2$- H$_2$O$_2$ system was greatly enhanced, the production of ·OH was almost not increased (Figure 4A). $^1$O$_2$ was derived from ·OH so it could refer that there was no increase in $^1$O$_2$ quantity. Ethanol was reported to react with ·OH and yield an octet spectrum that was completely distinct from the DMPO-OH spectrum (Finkelstein et al., 1980). The octet spectrum in the LaF$_3$:Ce NPs-NaNO$_2$- H$_2$O$_2$ system rooted in the reaction between ·OH and residual ethanol from treatment process of LaF$_3$:Ce NPs. Furthermore, AA, which was a scavenger for O$_3^-$, obviously inhibited the CL of the LaF$_3$:Ce NPs-NaNO$_2$- H$_2$O$_2$ system (Figure 4B). All the results indicated that O$_3^-$ was the critical reason for the enhanced CL instead of ·OH and $^1$O$_2$. O$_3^-$ acting as an electron donor reacted with LaF$_3$:Ce NPs to produce LaF$_3$:Ce NPs$^-$ (Equation 6) (Poznayak et al., 2004). ONOOH serving as a hole injector converted LaF$_3$:Ce NPs to LaF$_3$:Ce NPs$^+$ (Equation 7). Electron–hole annihilation between LaF$_3$:Ce NPs$^-$ and LaF$_3$:Ce NPs$^+$ resulted in CL emission (Equation 8) (Figure 5; Ding et al., 2002;
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FIGURE 3 | CL kinetic study of the LaF$_3$:Ce NPs-NaNO$_2$-H$_2$O$_2$ system. (A) CL kinetic curves of the LaF$_3$:Ce NPs-NaNO$_2$-H$_2$O$_2$ system with different reagent mixing orders: 1. injecting LaF$_3$:Ce NPs into the mixture of NaNO$_2$ and acidified H$_2$O$_2$; 2. injecting NaNO$_2$ into the mixture of LaF$_3$:Ce NPs and acidified H$_2$O$_2$; 3. injecting acidified H$_2$O$_2$ into the mixture of LaF$_3$:Ce NPs and NaNO$_2$. CL signals of three repeated experiments were given. (B) CL kinetic curves of the NaNO$_2$-H$_2$O$_2$ system and the LaF$_3$:Ce NPs-H$_2$O$_2$ system. Conditions: 3.00 M H$_2$O$_2$ in 0.04 M H$_2$SO$_4$, 50 µl of LaF$_3$:Ce NPs and 10 µM NaNO$_2$ solution. Voltage of the PMT was set at 1.2 kV.

FIGURE 4 | CL mechanism study of the LaF$_3$:Ce NPs-NaNO$_2$-H$_2$O$_2$ system. (A) EPR spectra of ·OH generated via the reaction of DMPO probe in the LaF$_3$:Ce NPs-NaNO$_2$-H$_2$O$_2$ and NaNO$_2$-H$_2$O$_2$ systems. (B) CL profiles of the LaF$_3$:Ce NPs-NaNO$_2$-H$_2$O$_2$ system with and without AA. Conditions: 3.00 M H$_2$O$_2$ in 0.04 M H$_2$SO$_4$, 50 µl of LaF$_3$:Ce NPs, 10 µM NaNO$_2$ solution, 12.4 µl of DMPO in 1 ml of H$_2$O, and 0.1 mM AA. Voltage of the PMT was set at 1.2 kV.

Poznyak et al., 2004; Zheng et al., 2009; Dong et al., 2010).

\[
\begin{align*}
\text{ONOOH} & \rightarrow \cdot\text{NO}_2^- + \cdot\text{OH} \\
\text{ONOOH} + \text{H}_2\text{O}_2 & \rightarrow \text{O}_2^- + \cdot\text{NO}_2^- + \text{H}^+ + \text{H}_2\text{O} \\
\text{O}_2^- + \cdot\text{OH} & \rightarrow \text{O}_2 + \cdot\text{OH}^- \\
\text{LaF}_3:\text{Ce NPs} + \text{O}_2^- & \rightarrow \text{LaF}_3:\text{Ce NPs}^- + \text{O}_2 \\
\text{LaF}_3:\text{Ce NPs} + \text{ONOOH} & \rightarrow \text{LaF}_3:\text{Ce NPs}^+ + \text{NO}_2^- + \text{H}_2\text{O} \\
\text{LaF}_3:\text{Ce NPs}^+ + \text{LaF}_3:\text{Ce NPs}^- & \rightarrow \text{LaF}_3:\text{Ce NPs}^* + \text{LaF}_3:\text{Ce NPs} \\
\text{LaF}_3:\text{Ce NPs}^* & \rightarrow \text{2LaF}_3:\text{Ce NPs} + \text{hv}
\end{align*}
\]

Nitrite Analysis

To establish the optimal conditions for nitrite analysis, the volume of LaF$_3$:Ce NPs added into the CL system and concentrations of H$_2$SO$_4$ and H$_2$O$_2$ were investigated, respectively. As shown in Figure 6A, 50 µl of LaF$_3$:Ce NPs was added into the CL system and provided the highest CL emission. Less LaF$_3$:Ce NPs inadequately reacted with ONOOH while surplus LaF$_3$:Ce NPs also consumed energy. Reactive substance ONOOH was the product of NaNO$_2$ and H$_2$O$_2$ in acid medium, so H$_2$SO$_4$ was indispensable for the CL system. No CL signals could be observed in the absence of H$_2$SO$_4$. The most intense
CL signal was obtained with the H$_2$SO$_4$ concentration of 0.04 M (Figure 6B). CL signal increased with the concentration of H$_2$O$_2$ in the range from 0 to 3.00 M (Figure 6C). Hence, the optimal analytical conditions for nitrite analysis were 3.00 M H$_2$O$_2$ in 0.04 M H$_2$SO$_4$ injected into the mixture of 50 µl of LaF$_3$:Ce NPs and nitrite solution.

Under the optimal conditions, CL signals for different nitrite concentrations were recorded and shown in Figure 7. Good linear relationship between CL intensity and nitrite concentration was obtained in the range from 1 to 100 µM with a correlation coefficient of 0.9981 ($y = 256.3x + 42.72$). The relative standard deviation values of the analysis were 8.7, 1.2, and 4.8% for nitrite concentrations of 1, 10, and 100 µM, respectively. The limit of detection ($S/N = 3$) for nitrite was 0.33 µM.

DISCUSSION

The eternal goals and challenges of analytical chemistry are developing accurate, automated, selective, stable, sensitive, high-speed, high-throughput, and in situ analytical methods and protocols (Ju, 2013). The combination of analytical chemistry with new materials, especially nanomaterials, is the current frontier research topics and exhibits greatly improved analytical capacities. CL analysis is a traditional analytical technology and possesses outstanding advantages, such as low cost, simple instrument, fast response, and high compatibility. The application of nanomaterials in CL analysis leads to new CL sensing disciplines and offers a broad palette of opportunities for analytical chemists. In 2004, Poznyak et al. (2004) firstly reported the nanocrystal band gap CL derived from CdSe/CdS core-shell QDs that acted as a novel class of luminophores with the emission state originated from quantum-confined orbitals. Superior emission properties in QDs gave promises for developing QD-based nanoprobes for CL analysis. Besides traditional semiconductor QDs, some novel nanomaterials, such as carbon nanodots (Lin et al., 2011), graphene QDs (Hassanzadeh and Khataee, 2018), graphitic carbon nitride QDs (Zhu et al., 2019), and N-dots (Zheng et al., 2017), were developed to be potential platforms for CL analysis.
sensing. These nanomaterials are superior in terms of robust chemical inertness, low toxicity, good aqueous solubility, high resistance to photobleaching, and satisfactory biocompatibility. Our work is an endeavor step during the development process of nanomaterial-sensitized CL analysis methods. In this study, LaF$_3$:Ce NPs were successfully synthesized and applied in nitrite detection based on CL signals. The synthetic process of LaF$_3$:Ce NPs was simple and the products were fully characterized to give indications for the CL mechanism study. The enhancement of LaF$_3$:Ce NPs for the NaNO$_2$–H$_2$O$_2$ CL system was efficient and the mechanism was systematically and scientifically explained. The linear relationship between CL intensity and nitrite concentration was found, although there were spaces for improving the limit of detection. This work tried to explore new CL nanoprobes and gave a new route for fluoride applications. In the future, there is still a great demand for developing novel CL nanoprobes especially metal-free QDs and two-dimensional QDs.

**CONCLUSIONS**

In summary, LaF$_3$:Ce NPs were successfully synthesized and demonstrated to intensely enhance ultra-weak CL of the NaNO$_2$–H$_2$O$_2$ system. The CL mechanism was suggested to be the electron–hole annihilation between hole-injected and electron-injected LaF$_3$:Ce NPs. The new CL system was developed to be a novel, simple, and straightforward analytical method for nitrite. All the experimental conditions were optimized and a satisfactory linear relationship between CL intensity and nitrite concentration was obtained. This work shed a new light on the research and application of traditional fluoride NPs doped with RE$^{3+}$.

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**DATA AVAILABILITY STATEMENT**

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation, to any qualified researcher.

**AUTHOR CONTRIBUTIONS**

YuW organized and conducted all the experiments, analyzed data, and wrote the manuscript. JW coordinated the project, supervised all the experiments, analyzed data, and wrote, edited, and reviewed the manuscript. YaW assisted the experiments of nitrite analysis. CH synthesized and characterized LaF$_3$:Ce NPs. TC performed experiments of the CL study of the LaF$_3$:Ce NPs–NaNO$_2$–H$_2$O$_2$ system. All authors contributed to the article and approved the submitted version.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.