Red Zn$_2$SiO$_4$:Eu$^{3+}$ and Mg$_2$TiO$_4$:Mn$^{4+}$ nanophosphors for on-site rapid optical detections: Synthesis and characterization

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Abstract

This study reports the synthesis and characterization of the red nanophosphors Zn$_2$SiO$_4$:Eu$^{3+}$ (ZSO:Eu$^{3+}$) and Mg$_2$TiO$_4$:Mn$^{4+}$ (MTO:Mn$^{4+}$). The use of phosphors as a fluorescence label for lateral flow immunochromatographic assay (LFIA) has also been described. The optimal photoluminescence (PL) for ZSO:Eu$^{3+}$ was obtained when it was synthesized with 7 mol% of Eu$^{3+}$ and annealed at 1100 °C for 1 h. Long fluorescence lifetime (1.01 ms), high activation energy $E_a$ (0.28 eV), and low PL degeneration (10% at 110 °C) are the characteristics of ZSO:Eu$^{3+}$. MTO:Mn$^{4+}$ also exhibited high PL intensity along with a high $E_a$ of 0.32 eV. The emission wavelengths of phosphors are biocompatible with the optical bio-window of tissues. When human immunoglobulin G (human IgG) at a constant concentration of 100 μg/mL was used for detection, the PL ratios of the test line to the control line were 2.15 and 2.28 for the ZSO:Eu$^{3+}$- and MTO:Mn$^{4+}$-labeled LFIA, respectively. Thus, the ZSO:Eu$^{3+}$ and MTO:Mn$^{4+}$ nanophosphors are capable of human IgG recognition and are the promising candidates as fluorescent labels for on-site rapid optical biodetection.

Graphical abstract

Keywords Nanophosphor · Fluorescence label · Biodetection

Extended author information available on the last page of the article
1 Introduction

In recent years, severe infectious diseases, such as COVID-19, have posed a significant risk to human health and have resulted in global economic crisis. This problem has prompted widespread concern, and many strategies have been proposed and developed for the detection and mitigation of various diseases. Approaches that can rapidly screen infectious viruses are expected to provide timely essential medical treatment to infected people and inhibit the proliferation of the virus. Lateral flow assays (LFAs) are a promising biological identification technique for the rapid detection of multiple analytes [1–8]. High sensitivity and stability, excellent portability, and high ability to provide point-of-care testing (POCT) are the advantages of LFAs.

LFAs are designed for visual inspection using a sample pad, conjugate pad, nitrocellulose (NC) membrane, absorption pad, and plastic backing. In LFA-enabled immunoassays, known as lateral flow immunochromatographic assays (LFIA) [1–5, 9–12], the sample pad contains the analyte, such as human immunoglobulin G (human IgG). On the conjugate pad, proteins (e.g., goat anti-human IgG) are labeled with fluorophores to form conjugated chromatic groups that are used as biological probes to identify the analyte. A test line (T-line) and control line (C-line) are prepared on the NC membrane for analyte investigation.

Two mechanisms govern the functionality of the LFIA. The first mechanism is the immunocompatibility between the analyte (antibody or antigen) and the biological probe (antigen or antibody). The other mechanism is the capillarity that propels the liquid flow in the assay. When the analyte–biological probe composites reach the NC membrane, they are collected in the T-line. The remaining uncoupled fluorophore probes continue to flow to the C-line; they are subsequently captured. By analyzing the fluorescence intensity ratio of the T-line to the C-line, the analyte can be identified, and its concentration can be determined. LFIA can quickly identify analytes without the need for specialized and costly equipment. This approach is suitable for clinical diagnostics at homes, point-of-care units, and laboratories and has attracted widespread attention.

Fluorophore labeling plays a vital role in analyte identification; it also influences the detection sensitivity of LFIA. Common fluorophore labels include colloidal gold nanoparticles (NPs) [13–19], colored latex beads [20, 21], magnetic NPs [18, 22, 23], carbon NPs [24–26], organic/inorganic particles [27, 28], and quantum dots (QDs) [29–33]. Table 1 lists the label species and their associated characteristics for preliminary screening using LFIA. Colloidal Au NPs have been broadly used for aflatoxin B1 to ensure the safety of food [11]; Hg²⁺ detection has been used for environmental monitoring [15]. However, the surface of the Au NPs is not stable under high salt concentrations [26].

A stable detection performance is observed for LFIA labeled with magnetic NPs. However, magnetoresistive LFIA requires a readout system for magnetic signal analysis [34]. Multi-walled carbon nanotubes (MWCNTs) are another conventional label for LFIA. These labels provide a high specific surface area for the immobilization of identification probes, although CNTs should be functionalized first to mitigate aggregation and improve solubility [26].

In recent years, luminescent NPs have attracted attention as labels for LFIA owing to the development of inorganic

| Nanoparticles            | Target analytes                      | Detection limit | Ref  |
|--------------------------|--------------------------------------|-----------------|------|
| Au nanoflowers           | Aflatoxin B1                         | 0.32 pg mL⁻¹    | [11] |
| Hierarchical flowerlike Au NPs | Escherichiacoli O157:H7         | H7103 CFU mL⁻¹  | [13] |
| Au NPs                   | Hg²⁺                                | 0.0015 ppb      | [15] |
| Au NPs                   | Lead ions                           | 0.19 ng mL⁻¹    | [16] |
| Au NPs                   | Ciprofloxacin                       | 5 ng mL⁻¹       | [17] |
| Magnetic NPs             | Salmonella enteritidis              | 1.95 × 10⁵ CFU mL⁻¹ | [18] |
| Magnetic NPs             | Bacillus anthracis spores           | 500–700 spores  | [22] |
| Carbon dots (CD)/Ag NPs  | Enrofloxacin                        | 0.1 μg L⁻¹      | [24] |
| Amorphous carbon NPs     | Zearealenone                        | 1 μg kg⁻¹       | [25] |
| MWCNTs                   | Hg²⁺                                | 0.05 ppb        | [26] |
| Dye-doped silica NPs     | Enrofloxacin                        | 0.02 ng mL⁻¹    | [27] |
| CdS/ZnS QDs              | N-terminal pro-B-type natriuretic peptide | 50 pg mL⁻¹ | [29] |
| CdTe/ZnS QDs             | Rhein                               | 98.2 ng mL⁻¹    | [30] |
| Cu:Zn – In – S/ZnS QDs   | Tetanus Antibody                    | 0.001 IU mL⁻¹   | [31] |
| CdSe/ZnS QDs             | Mite allergens                      | 0.087 IU mL⁻¹   | [33] |
nanophosphors. Semiconductor emissive QDs, such as CdS/ZnS QDs [29], Cu:Zn – In – S/ZnS QDs [31], and CdSe/ZnS QDs [33] are examples of luminescent NPs. CdSe/ZnS QDs show color-tunable emission and have been used to detect mite allergens [33] and gastric cancer carbohydrate antigens 72–4 [35]. Human chorionic gonadotrophin (HCG) was also detected using CdSe/ZnS QDs labeled LFIA; the HCG detection limit was 0.5 IU/L in a detection time of 10 min [36]. However, high toxicity is a limitation of CdSe-based QDs used for biodetections.

NPs of inorganic nanophosphors are also potential luminescent labels [2, 37–41]; they possess unique features such as tunable up/down-conversion luminescence and high chemical stability; moreover, they are easily functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized [2, 40]. The down-conversion carboxyl-capped YVO₄:Eu, Bi has been used as a label for the functionalized.

Inorganic nanophosphors Zn₂SiO₄:Eu³⁺ (ZSO:Eu³⁺) and Mg₂TiO₄:Mn⁴⁺ (MTO:Mn⁴⁺) exhibit a long fluorescence lifetime, high chemical and physical stability, and low toxicity. In addition, ZSO:Eu³⁺ exhibits unique red to near-infrared (NIR) luminescence. These features demonstrate their suitability for applications in biosensors. Accordingly, in this study, red ZSO:Eu³⁺ nanophosphor was synthesized for use as a fluorescent label for LFIA. An MTO:Mn⁴⁺-labeled LFIA was prepared as a control group. A nanophosphor-labeled LFIA for human IgG detection is presented.

2 Experimental

The Zn₂SiO₄:Eu³⁺ phosphor was prepared via the sol–gel method. Zn(NO₃)₂·6H₂O (99%; Alfa), tetraethoxysilane (TEOS, 98%; Acros), and Eu(CH₃COOH)₃ (99.9%; Alfa) were used as the raw materials. The concentration of Eu³⁺ was varied from 1 to 9 mol%. First, the raw materials were weighed according to their stoichiometric ratios. TEOS, anhydrous alcohol (99.5%; CH₂OH), and deionized (DI) water were mixed in a weight ratio of 2:2:1 to form solution A. Solution B was prepared by mixing Eu(CH₃COOH)₃ with DI water. Solutions A and B were blended and homogenized by stirring for 30 min. This homogenized solution was subsequently catalyzed with HCl, stirred for 30 min, and dried in an oven at 120 °C. Finally, the obtained powder was annealed at 800–1300 °C for 1 h for phosphor synthesis.

The MTO:Mn⁴⁺ phosphor was prepared via a citric acid-assisted sol–gel process using the following raw materials: Mg(NO₃)₂·6H₂O (99%; Acros), Ti(OCH₂)₄ (99%; Alfa), Mn(NO₃)₂·4H₂O (Acros), citric acid C₃H₅(OH)₃ (99.5%; Showa), anhydrous alcohol C₂H₅OH (99.5%; ECHO), and DI water [46]. When the MTO:Mn⁴⁺ was doped with 0.1 mol% of Mn⁴⁺ and annealed at 1300 °C for 5 h, the highest red luminescence was obtained.

The crystallinity of the phosphors was investigated using X-ray diffraction (XRD) with a Siemens D5000 X-ray powder diffractometer. The morphology and elemental composition were analyzed using field-emission scanning electron microscopy (SEM; JEOL 6330). The photoluminescence (PL) and PL excitation (PLE) spectra and the lifetime of the phosphors were determined using a Hitachi F-7000 spectrometer equipped with a 150-W xenon lamp.

The LFIA stripe was assembled according to the process reported by Luo et al.[2]. The reagents included 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC, 97%, Acros), N-hydroxysuccinimide (NHS, 98%, Alfa), phosphate buffer saline (PBS, 10x, UniRegion Bio-Tech), polyoxyethylene sorbitan monolaurate (Tween 20, Sigma-Aldrich), and sucrose (J.T. Baker). Human IgG at a constant concentration of 100 µg/mL was used as the analyte.

First, phosphor (12 mg), EDC (24 mg), NHS (24 mg), and goat anti-human IgG (0.36 mg) were dispersed in PBS (0.01 M, pH 7.2). This mixture underwent ultrasonic vibration at 4 °C for 2 h and allowed to stand overnight. Subsequently, the solution was centrifuged for 30 min. After removing the supernatant, the precipitate was dialyzed for 24 h against the dialysis buffer solution (0.1 M PBS, 3 wt% BSA, 10 wt% sucrose, and 0.25 wt% Tween 20) to remove unbound phosphors and antibodies. The obtained bio-conjugates of phosphor coupled with goat anti-human IgG were diluted to 1.0 mg/mL and then sprayed onto the conjugated pad.

The NC membrane was sprayed with 1.0 mg/mL rabbit anti-human IgG and 2.0 mg/mL human IgG, individually to form parallel T- and C-lines. Finally, the sample pad, conjugate pad, NC membrane, absorption pad, and plastic backing were assembled into an LFIA stripe. Rabbit anti-human IgG that was sprayed on the T-line was used to trap human IgG-conjugated fluorophore probes. For analyte recognition, the fluorophores of phosphor-labeled bio-conjugates on the T- and C-lines were excited by a UV lamp (UVGL-58, 5 W, 1350 mW/cm²) at a wavelength of 365 nm, and their PL spectra were measured using a spectroradiometer PR-655. From the analysis of the PL intensity ratio measured from the T- and C-lines, the analyte can be screened and identified.
3 Results and discussion

Because the characteristics of the control molecule, MTO:Mn$^{4+}$ phosphor, were described [46], this study only investigated the crystallization and luminescence properties of the ZSO:Eu$^{3+}$ nanophosphor. Figure 1a shows the XRD patterns of ZSO:Eu$^{3+}$ doped with different Eu$^{3+}$ concentrations and synthesized at 1100 °C for 1 h. The crystalline structure of the ZSO:Eu$^{3+}$ matched well the standard single-phase willemite (rhombohedral) structure of Zn$_2$SiO$_4$ (JCPDS No. 37–1485), with space group of $R$–$3$ and cell constants $a = b = 13.94$ Å, $c = 9.31$ Å [47–49]. The values of the full width at half maximum (FWHM, $\Delta 2\theta$) of the (410) peak were 0.193, 0.192, 0.191, 0.190, and 0.191° when the ZSO:Eu$^{3+}$ was doped with 1, 3, 5, 7, and 9 mol% of Eu$^{3+}$, respectively, as shown in Fig. 1b. The crystallinity of the phosphor was not altered significantly even when it was doped with a high Eu$^{3+}$ concentration of 9 mol%. The effects of the synthesis time and temperature on the crystallization of ZSO:Eu$^{3+}$ are shown in Fig. 1b. Herein, the Eu$^{3+}$ concentration of 9 mol% was used to optimize the synthesis time (1 h) and temperature (1000 °C). As compared with variation in Eu$^{3+}$ concentration, the FWHM value of (410) peak varied considerably with variations in the synthesis time and temperature. When the smallest FWHM value was obtained, the best crystallization of ZSO:Eu$^{3+}$ was achieved. Consequently, the optimal synthesis conditions for Eu$^{3+}$ doping concentration, synthesis temperature, and time were 7 mol%, 1100 °C, and 1 h, respectively.

The morphologies of ZSO:Eu$^{3+}$ are shown in Fig. 2a–c and Fig. S1 (Online Resource). It can be observed that the phosphors were synthesized with irregular particle morphologies. Most of the particles are dispersed; however, some may aggregate to form larger particles. The particle size distribution of ZSO:Eu$^{3+}$ analyzed by SEM was determined to be approximately 300–400 nm. The crystallite size was also estimated from the XRD (410) peak using the Scherrer formula [50, 51]. The calculated crystallite size of ZSO:Eu$^{3+}$ was 430–437 nm, which was comparable to the result of SEM analysis. The slight difference in the size of ZSO:Eu$^{3+}$ analyzed by XRD and SEM is attributed to the fact that one obtains the mean size of the crystallite, whereas the other shows the morphological particle. The elemental composition of ZSO:7 mol% Eu$^{3+}$ was analyzed using energy-dispersive X-ray spectroscopy (EDS). Figure 2c shows the EDS image obtained from the square area in Fig. 2b. EDS analyses in different areas of ZSO:7 mol% Eu$^{3+}$ are also shown in Fig. S2 (Online Resource). The analyzed compositions of Zn, Si, O, and Eu were approximately 27.20, 17.28, 54.67, and 0.85 at%, respectively, which were in good agreement with their theoretical values of 27.57, 14.30, 57.14, and 0.99 at%, respectively.

The binding energies of the elements in the ZSO:Eu$^{3+}$ crystal were analyzed using XPS. Figure 3 shows a peak at 532.9 eV, which is attributed to the O 1 s band [52, 53]. The Si 2p and Si–O peaks are at 99.7 and 103.4 eV, respectively [53–55]. The characteristic Zn peaks, 2p$_{3/2}$ and 2p$_{1/2}$, were observed at 1021 and 1045 eV, respectively [56, 57]. A broad Eu 4d peak was observed at approximately 135.4 eV [52, 58, 59], which shows that Eu$^{3+}$ was doped into the ZSO crystal.

The energy absorption and emission characteristics of ZSO:Eu$^{3+}$ were analyzed from PLE and PL spectra at an excitation wavelength ($\lambda_{\text{ex}}$) of 394 nm and emission wavelength ($\lambda_{\text{em}}$) of 616 nm, as shown in Fig. 4a. The
Fig. 2  a–c SEM images and d EDS spectrum of ZSO:Eu$^{3+}$ phosphor

Fig. 3  XPS spectra of Zn, Si, O, and Eu in ZSO:Eu$^{3+}$

Fig. 4  PL and PLE spectra of a ZSO:Eu$^{3+}$ and b MTO:Mn$^{4+}$ phosphors
maximum energy absorption and emission peaks were observed at wavelengths of 394 and 616 nm, respectively, which were attributed to electron transitions from $^7F_0$ to $^5L_6$ and $^5D_0$ to $^7F_2$ in Eu$^{3+}$, respectively [60–63].

In addition to the energy absorption and emission characteristics, thermal stability is an important property, relative to the thermal degradation characteristics of phosphors. Accordingly, the luminescence of the as-prepared phosphors was analyzed at a low temperature range of 30–110 °C, considering the phosphors for biosensor applications. Figure 5a shows the PL spectra of the ZSO:Eu$^{3+}$ phosphor heated at different temperatures. The PL patterns were similar, and the change in emission color was insignificant when the temperature was increased. A highly stable luminescence was also observed; a negligible change in PL intensity, less than 10%, was measured when the heating temperature was increased from 30 to 110 °C (Fig. 5b). The thermostability of the phosphor can also be analyzed using the Arrhenius equation expressed as

$$\ln\left[\frac{I_0}{I(T)} - 1\right] = \ln A - \frac{E_a}{kT}$$

where $I_0$ is the PL intensity at the initial temperature, and $I(T)$ is the PL intensity at temperature $T$. $A$ is the pre-exponential factor, $k$ is the Boltzmann constant, and $E_a$ is the activation energy for the thermal quenching of the phosphor. From the thermometric measurement of the phosphor, a plot of $\ln\left[\frac{I_0}{I(T)} - 1\right]$ versus $(kT)^{-1}$ was obtained. This plot shows a linear relationship between $\ln\left[\frac{I_0}{I(T)} - 1\right]$ and $(kT)^{-1}$, as shown in Fig. 5c. The $E_a$ value calculated from the slope was 0.28 eV. This high $E_a$ property leads to the high thermal stability of the ZSO:Eu$^{3+}$ phosphor.

Moreover, the lifetime ($\tau$) of the ZSO:Eu$^{3+}$ was deduced from the luminescence decay plot (Fig. 6) using Eqs. (1) and (2) as follows [64, 65]:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

$$\tau = \frac{(A_1 \tau_1^2 + A_2 \tau_2^2)}{(A_1 \tau_1 + A_2 \tau_2)}$$

where $\tau_1$ and $\tau_2$ are the components of the luminescence lifetime, and $A_1$ and $A_2$ are the fitting parameters. $I(t)$ is the emission intensity at time $t$. Thus, the calculated lifetime of the ZSO:Eu$^{3+}$ was 1.01 ms. The high thermal stability and long lifetime contribute to the ability of phosphors to resist photochemical degradation.

The optimal synthesis temperature, time, and Mn$^{4+}$ doping concentration of the red MTO:Mn$^{4+}$ phosphor were 1300 °C, 5 h, and 0.1 mol%, respectively [46]. The XRD pattern of the MTO:Mn$^{4+}$ phosphor is shown in Fig. S3 (Online Resource). The development of MTO:Mn$^{4+}$ crystals and the formation of a single-phase phosphor were facilitated when citric acid was added during the sol–gel process.

MTO:Mn$^{4+}$ also possesses a high activation energy of 0.32 eV and a fluorescence lifetime of 0.55 ms. The emission band of ZSO:Eu$^{3+}$ was in the range 605–725 nm, and that of MTO:Mn$^{4+}$ was in the 630–720 nm range, as shown
in Fig. 4b. Both phosphors showed a large wavelength shift between the absorption and emission bands. This distinctive feature of phosphors contributes to the significant alleviation of self-quenching caused by molecular self-absorption. In addition, ZSO:Eu³⁺ and MTO:Mn⁴⁺ emit in the red and NIR regions, and their NIR emission is biocompatible with the bio-window of tissues. Furthermore, low toxicity is a unique characteristic of ZSO:Eu³⁺ and MTO:Mn⁴⁺ phosphors (Figs. S4–S7, Online Resource). Thus, ZSO:Eu³⁺ and MTO:Mn⁴⁺ hold great promise for biodetection and diagnostic bioimaging applications.

To detect human IgG using the phosphor-labeled LFIA method, phosphor-conjugated goat anti-human IgG, rabbit anti-human IgG, and human IgG were sprayed on the conjugate pad, T-line, and C-line, respectively. The peak intensities of PL measured from the T-line and C-line were expressed as PL_T and PL_C, respectively.

Figure 7a shows the PL spectra measured from the T- and C-lines of the ZSO:Eu³⁺-labeled LFIA; herein, the excitation wavelength was set to 365 nm. A high PL_T-to-PL_C ratio of 2.15 was measured, which indicated that human IgG (100 μg/mL) could be detected and identified. The intensity ratio of PL_T to PL_C was 2.28 for the MTO:Mn⁴⁺-labeled LFIA, comparable to that of the ZSO:Eu³⁺-labeled LFIA. The peak intensities of PL measured from the T-line and C-line were expressed as PL_T and PL_C, respectively.

Figure 7b shows the PL spectra measured from the T- and C-lines of the ZSO:Eu³⁺-labeled LFIA; herein, the excitation wavelength was set to 365 nm. A high PL_T-to-PL_C ratio of 2.15 was measured, which indicated that human IgG (100 μg/mL) could be detected and identified. The intensity ratio of PL_T to PL_C was 2.28 for the MTO:Mn⁴⁺-labeled LFIA, comparable to that of the ZSO:Eu³⁺-labeled LFIA. The quantity of human IgG and the sensitivity of LFIA can be determined from the ratio of PL_T to PL_C [2].

Photographs of the LFIA stripes labeled with ZSO:Eu³⁺ and MTO:Mn⁴⁺ are shown in Fig. 7b, c, respectively. The red luminescence of the ZSO:Eu³⁺- and MTO:Mn⁴⁺-labeled LFIA can be clearly observed with the naked eye. Clearly, both ZSO:Eu³⁺ and MTO:Mn⁴⁺ are promising candidates as fluorescent labels for biological detection applications. However, there is still work to be done, including minimizing the particle size of phosphors, passivating the particle surface, elongating persistent luminescence, and enhancing NIR luminescence. The difficulty in acquiring sufficient biological resources is also a major challenge in achieving a detailed study.

### 4 Conclusions

For the ZSO:Eu³⁺ phosphor prepared via the sol–gel method, the optimal PL intensity was obtained when it was synthesized with 7 mol% Eu³⁺ and annealed at 1100 °C for 1 h. The particle size of ZSO:Eu³⁺ analyzed by SEM was approximately 300–400 nm. XPS analysis showed that Eu³⁺ was doped into the ZSO crystal. The compositions of Zn, Si, O, and Eu in the ZSO:0.07 Eu³⁺ were close to their theoretical values of 27.57, 14.30, 57.14, and 0.99 at%, respectively. In addition, the MTO:Mn⁴⁺ phosphor was prepared via a citric acid-assisted sol–gel process. The maximum luminescence of MTO:Mn⁴⁺ was obtained when the phosphor was doped with 0.1 mol% of Mn⁴⁺ and annealed at 1300 °C for 5 h.

High activation energy, long fluorescence lifetime, and biocompatible luminescence are characteristics of red ZSO:Eu³⁺ and MTO:Mn⁴⁺ phosphors. When the ZSO:Eu³⁺-labeled LFIA was used for human IgG detection, a high
PL$_2$–to–PL$_C$ ratio of 2.15 was obtained, which is comparable with the intensity ratio of 2.28, obtained from that of MTO:Mn$^{4+}$-labeled LFIA. This shows that ZSO:Eu$^{3+}$ and MTO:Mn$^{4+}$ as fluorescent labels have a high potential for LFIA applications.

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**Declarations**

**Conflict of Interest** The authors declare that they have no conflict of interest.

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