Internal Referencing Photoluminescence Probes for Simultaneous Sensing of O$_2$ Gas and Temperature Based on Mn:MAPb(Br/Cl)$_3$ Perovskite

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The ratiometric photoluminescence (PL)-based O$_2$ sensitive probes provide built-in self-calibration for the correction of various target-independent influencing factors. They attract particular attention to be used for O$_2$ gas sensing and imaging. Herein, internal referencing ratiometric PL probes are fabricated that not only detect O$_2$ concentration and temperature simultaneously but also remove the destructive effect of temperature on O$_2$ sensing. A dual-emission thin film of Mn-doped halide perovskite nanocrystals (PNCs) (Mn:MAPb(Br/Cl)$_3$) with a 50% PL quantum yield is used as the sensing layer, which is synthesized in situ. Through the sensing process, excitonic PL and the PL caused by Mn are used for detecting temperature and O$_2$ partial pressures, respectively. Remarkably, the Mn PL intensity shows 40% decrement with increasing O$_2$ partial pressures from 0% to 20%, while for the excitonic PL, intensity changes are less than 5%. As the temperature undesirably affects the sensing quantity, the O$_2$ PL is used as an internal reference signal to achieve good accuracy and selectivity. Furthermore, the temperature variation is determined by measuring PL peak intensity change and wavelength shift. In addition to the O$_2$ gas sensitivity of 1.55, a relative temperature sensitivity of $-9.36\%\,K^{-1}$ is also achieved.

1. Introduction

The development of oxygen (O$_2$) gas sensors has been extensively considered as they are used in many fields such as environmental pollution management, combustion process control in exhaust emission from the power plants, and biotechnological processes. The O$_2$ concentration in these devices is determined using different approaches such as optical and electrochemical methods, depending on the application. Among them, the optical ones are particularly attractive as they do not consume oxygen, which in turn provides reversibility, good precision, and accuracy with a fast response time. Furthermore, optical sensors can be fabricated in different sizes and structures, such as fiber-based ones, providing both remote and portable measurements. [1] A well-known approach, successfully industrialized for several years, is based on the quenching of the luminescence of the sensitive material in the presence of O$_2$ molecules. The response of these sensors, which relies on the approximate empirical models, also depends on other parameters related to the surroundings such as temperature, light intensity, and sensor position. Particularly, in addition to oxygen concentration, temperature strongly influences the measurement, as both the luminescence and the quenching phenomena are temperature dependent. [1,2] To remove these effects that cause inaccuracy in the sensor response, an inert reference fluorophore emission at a different wavelength is often used. [1,3] Using a single O$_2$ sensitive probe (OSP) with dual emissions that are differently quenched as the temperature rises is one of the effective approaches for overcoming the mentioned challenge. Generally, there are two techniques for fabricating internal referencing ratiometric OSPs. The first technique (single reference) introduces a second signal as a reference that is target insensitive. The other technique applies two target-responsive signals that show opposite responses, providing the achievement of dual-emission ratiometric PL. [3] There are two main methods utilized for the fabrication of dual-emission fluorophores. In the first one, the dual-emission structure is formed using two luminophore materials such as the materials with core/shell structure [4] and embedded nanocrystals (NCs)—organic and inorganic dyes. [5] In the other method, an intrinsically dual-emission fluorophore material is used such as doped NCs [6] and organic dyes. [7] Single-fluorophore dual-emission facilitates the development of a simplified ratiometric design. In comparison with the organic and inorganic dyes-based dual-emission fluorophore materials, doped NCs’
dual-emission fluorophores exhibit broader absorption spectra and narrower emission peaks. In addition, doped NCs-based dual-emission fluorophores possess high PL quantum yield (PLQY), long-term photostability, tunable emission, low cost, and easy fabrication.[1,8] Wu et al. developed an OSP based on multiple fluorophores including inorganic perovskite nanocrystals (PNCs) and PtTFPP (platinum(II)-5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)-porphyrin) dye. As they reported, the PtTFPP emission intensities decreased inversely with O2 partial pressure. The relative fluorescence intensity of PNCs was insensitive to O2, indicating the PNCs are suitable to be used as the internal reference for O2 gas sensing.[5] Lin et al. used the Mn-doped CsPbCl3 single fluorophore based on dual-emission NCs for sensing of O2 by means of host-dopant energy transfer.[9] This kind of PL-based sensory design has extensively been considered by researchers[6,10] because the doping of Mn2+ ions into the host NCs provides a new direction for exciton energy transfer. It should be noted that one of the main challenges of the halide perovskites is their instability against moisture, which plays a key role in all their applications such as O2 gas sensing. Thus far, several strategies have been developed to overcome this limitation though it still needs more study. When perovskite crystals contact with water molecules, degradation occurs and subsequently their sensitivity is lost. For instance, covering with an appropriate polymer is one of the strategies that has been considered in some works. Amjadi et al. embedded PNCs in polydimethylsiloxane (PDMS) as a hydrophobic polymer which efficiently protected them against moisture.[11] Casanova-Cháfer et al. developed a gas sensor based on MAPbBr3 PNCs that was protected against moisture using a thin hydrophobic layer of graphene.[12]

The dual-emission PL spectrum derived from single-exciton band-edge absorption implies the presence of intraparticle host dopant energy transfer (HDET) in PNCs.[13] Mn-doped PNCs are promising materials for O2 sensing due to their unique phosphorescence emission (near 580–615 nm), long phosphorescent lifetime, large Stokes shift, and paramagnetic property. Due to the feasible electronic energy transfer from their long-lifetime excited state to the triplet ground state of O2, the phosphorescent dopants such as Mn2+ can act as PL OSPs. Such a mechanism behind the inherent O2 sensing capability results in the rapid and reversible phosphorescence dimming of Mn2+ emission.[9] Huang et al. fabricated a dual-emission ratiometric temperature sensor based on Mn-doped CsPb(Cl/Br)3 NCs. Through this sensing, as the temperature rose from 5 to 50 °C, the intrinsic emission intensity of PNCs at 440 nm decreased gradually, and the emission peak redshifted due to the thermally activated trapping of charge carriers and the thermal expansion of the crystalline lattice. However, the emission from Mn dopants (572 nm) showed the opposite behavior. This peak blueshifted with increasing temperature due to the thermal expansion of the crystalline lattice. As reported, the Mn PL intensity enhancement is because of the overlap between the emission spectra of perovskite and Mn, where the elevated temperature promoted the energy transfer between perovskite (donor) and Mn (acceptor).[14] Thus far, in almost all of the reported works, PNCs and Mn-doped ones have been synthesized using colloidal methods. In addition to the high temperatures needed for these methods, PNCs should be extracted and purified before being used as OSPs, making the process more complex and time-consuming.

In this work, internal referencing ratiometric PL probes are fabricated based on Mn-doped PNCs for simultaneous sensing of O2 molecules and temperature with high accuracy. To fabricate the sensing probes, the dual-emission Mn:MAPb(Br/Cl)3 PNC layer is synthesized in situ through a facile solution-based method. In this method, poly(vinylpyrrolidone) (PVP) is used as a grain size controller and defect-passivating molecule, leading to the formation of PNCs with a high PLQY. The composition of the sensing layer is engineered to remove the destructive effect of the temperature on O2 gas detecting. The crystalline, morphological, and optical properties of the PNCs are investigated and tuned to achieve the best sensing performance. Also, the response of the sensing probes is studied optically and compared with the literature.

2. Result and Discussion

To achieve a uniform sensing layer with low defect density and high quantum efficiency, the morphology and size of the perovskite grains are controlled using PVP. As clearly observed in the field-emission scanning electron microscopy (FESEM) images (Figure 1a,b), a uniform layer of PNCs is formed when 30 wt% PVP is added into the perovskite precursor. The transmission electron microscopy (TEM) image presented in Figure 1c confirms the formation of spherical-shaped MAPb(Br/Cl)3 NCs with an average size of 18 nm (Figure S1, Supporting Information). To define the optimum percentage of PVP for achieving small-sized and high-quality PNCs, the effects of different amounts of PVP including 13, 19, 27, 30, 33.5, and 36 wt% are investigated (Figure S2a–c, Supporting Information). As explained in the Supporting Information, with increasing PVP concentration, the crystallite size decreases. Though PNCs with smaller sizes result when the PVP wt% is higher than 30%, the PL intensity shows a descending trend. It results from Figure S2d, Supporting Information, which shows that the highest intensity is achieved for the exciton PL of the sample with 30 wt% PVP. For PVP concentrations higher than 30 wt%, the PL intensity declines. Thus, 30 wt% PVP is considered as the optimum level for achieving high-quality and defect-free PNCs.

To investigate the effect of PVP on the crystalline structure of undoped MAPb(Cl/Br)3 films, the X-ray diffraction (XRD) diffraction patterns are depicted in Figure 1d. The major diffraction peaks located at 15.6°, 31.4°, and 47.88° correspond to (100), (210), and (300) planes, revealing the formation of cubic perovskite structures in both pure and PNC films. For a better understanding of the effect of the PVP on the crystallite size of the synthesized PNCs, the average crystallite sizes are calculated from the Debye–Scherrer equation (Equation S1. Supporting Information) using the most intense peak, (100). The full width half maximum (FWHM) of the (100) peak is calculated by fitting the peak with a Lorentz distribution function for obtaining the lattice parameters (a = b, c) and cell volume of the layers. As summarized in Table S1, Supporting Information, the FWHM increases from 0.0948° to 0.2952° when 30 wt% PVP is added into the precursor. It indicates the significant reduction of the crystallite size from 68 to 26 nm.
To achieve a dual-emission probe, the perovskite film is doped with Mn$^{2+}$.

Figure 2a–c shows the FESEM images of MAPb(Br/Cl)$_3$ PNCs comprising different ratios of Mn/Pb for PbBr$_2$/(PbBr$_2$ + PbCl$_2$) = 2/10. It clearly shows that the morphology and the quality of films are strongly dependent on the ratio of Mn/Pb. A comparison of the morphology of the undoped PNC film (Figure 1b) and the doped ones (Figure 2a–c) indicates that the Mn doping affects the uniformity of MAPb(Cl/Br)$_3$ film undesirably. To achieve high quality Mn-doped PNCs and remove unreacted precursors in the synthesized film, annealing treatment at 130 $^\circ$C for 10 min is performed subsequently after film deposition. A comparison of the FESEM images of Mn-doped MAPb(Br/Cl)$_3$ PNCs with the ratio of Mn/Pb = 9/1 before and after annealing indicates that the quality of the annealed film is significantly improved.

The XRD patterns of the films with different dopant concentrations prepared at room temperature are presented in Figure 3. For the nominal doping concentration of Mn$^{2+}$ in the range of 0–4/6 Mn/Pb (MnCl$_2$/(PbBr$_2$ + PbCl$_2$)) ratios, the XRD diffraction peaks can be attributed to the cubic-phase Mn:MAPb(Cl/Br)$_3$ perovskite structure (space group: Pm3m), demonstrating the negligible effect of the incorporation of Mn$^{2+}$ on the crystal structure of MAPb(Cl/Br)$_3$.$^{[15]}$ For the high-level doping concentrations of Mn$^{2+}$ (8/2–9/1 Mn/Pb ratios), diffraction peaks corresponding to CH$_3$NH$_3$Cl and MnCl$_2$ precursors can be clearly detected, signifying the presence of unreacted precursors in the formed films. Moreover, according to Figure 3b, for the high-level doping concentration (Mn/Pb = 9/1), the FWHM increases from 0.257° to 0.682° after thermal annealing, representing the significant reduction of the crystallite size from 30 to 12 nm, which is consistent with the TEM results (Figure S3, Supporting Information). After thermal annealing, the diffraction peaks corresponding to CH$_3$NH$_3$Cl and MnCl$_2$ precursors are completely removed. Figure 3c shows the fitting of the XRD peak assigned to (100) planes with a Lorentz distribution function. The peak related to the doped PNCs shifts to a higher 2$\theta$ ($\Delta 2\theta = 0.1^\circ$) and broadens compared with that of the undoped one, indicating the incorporation of smaller Mn ions into the lattice sites of Pb ions in Mn:MAPb(Cl/Br)$_3$, confirming the successful doping of PNCs by Mn.

Figure 4 shows the energy dispersive X-ray (EDX) spectra of undoped and doped (Mn/Pb = 9/1) PNCs, respectively, confirming the presence of Pb, Cl, and Br in the undoped film and Pb, Cl, Br, and Mn in the doped film. Moreover, as observed, the detected ratio of Mn/(Pb + Mn) in the doped sample is consistent with the stoichiometric ratio (Mn/(Pb + Mn) = 0.9) used in the precursor solution.

The optical behavior of the prepared films in the presence of the 30 wt% PVP and also different concentrations of Mn for PbBr$_2$/(PbBr$_2$ + PbCl$_2$) = 2/10 is presented in Figure 5. According to the absorption plots of the perovskite with and without PVP (Figure 5a), a blueshift occurs in the presence of

![Figure 1](image1.png)

Figure 1. FESEM images of as-prepared undoped MAPb(Cl/Br)$_3$ for PbBr$_2$/(PbBr$_2$ + PbCl$_2$) = 2/10 a) without PVP, b) with PVP, and c) TEM image of MAPb(Br/Cl)$_3$ PNCs with PVP. d) The XRD pattern of MAPb(Cl/Br)$_3$ film with and without PVP.
polymer chains (PVP). The optical $E_g$ about 3.075 eV is achieved for the PNCs while this value for the pure film is 2.6 eV. The size reduction in the presence of PVP is the reason for the observed blueshift of the bandgap, which can be attributed to the quantum confinement effect in the NCs.

As shown in Figure 5b, in the Mn-doped MaPb(Br/Cl)$_3$ films, a redshift in the optical bandgap is observed with increasing Mn/Pb ratio. For Mn/Pb ratios of 4/6, 8/2, and 9/1, the achieved $E_g$ is 3.05, 2.95, and 2.9 eV, respectively. The incorporation of smaller Mn-ion size (70 pm) into the lattice sites of Pb (119 pm) ions in Mn:MAPb(Cl/Br)$_3$ can induce compressive strain because of the lattice mismatch. Thus, the bandgap redshift in the doped sample can be addressed to the compressive strain induced in the presence of Mn,

Regarding the PL (Figure 6a), the highest intensity is achieved for the excitonic PL of the sample with Mn/Pb = 4/6 ratio. It reveals that in this composition, more qualified crystallinity is achieved, which is consistent with the XRD results shown in Figure 3. In contrast, for higher concentrations of Mn (Mn/Pb = 8/2 – 9/1), the achieved excitonic PL intensity is lower than the PL intensity of Mn/Pb = 4/6 ratio. In addition, there is a clear increase in the intensity of Mn emission at 614 nm, as a result of the higher Mn doping concentration (Figure 6a,b). The lower intensity of excitonic PL in highly doped PNCs can be ascribed to the enhanced intersystem
The PL intensity of Mn$^{2+}$ emission in the doped PNCs is strongly dependent on the amount of Br and Cl available in the structure and Mn doping concentration. To control Mn$^{2+}$ PL intensity, we prepare perovskite precursor solution with constant Mn/Pb = 1/9 ratio, 30 wt% PVP, and different ratios of PbBr$_2$/(PbBr$_2$ + PbCl$_2$). The PbBr$_2$/(PbBr$_2$ + PbCl$_2$) precursor ratios are engineered to achieve a high Mn PL intensity for doped PNCs. The PL spectra of Mn:MAPb(Br/Cl)$_3$ films with different ratios of PbBr$_2$/(PbBr$_2$ + PbCl$_2$) are shown in Figure 7. The intensity of Mn$^{2+}$ emission in the doped NCS shows an ascending trend with increasing Br composition and reaches the maximum intensity at PbBr$_2$/(PbBr$_2$ + PbCl$_2$) ratio of 2/10 and then decreases with adding further Br.
The PLQYs of Mn-doped PNC samples with different Mn/Pb ratios and constant PbBr$_2$/(PbBr$_2$ + PbCl$_2$) = 2/10 are summarized in Table 1. The Mn-doped PNC film with the ratio of Mn/Pb = 9/1 results in a PLQY as high as 50% under continuous excitation at a wavelength of 405 nm.

To investigate the O$_2$ gas partial pressure and temperature-sensing behavior of the synthesized layer, at first, the interaction of the perovskite layer with O$_2$ molecules is considered at isothermal conditions. In this regard, Mn:MAPb(Cl/Br)$_3$ PNC sensing layer with the maximum doping ratio of 9/1 is exposed to different O$_2$ partial pressures in a designed chamber shown in Figure S4, Supporting Information. According to the PL spectra presented in Figure 8, when the atmospheric O$_2$ percentage (%) increases from 0 to 100%, the Mn$^{2+}$-related PL intensity quenches significantly, while the exciton emission shows a slight decrease. As can be observed, the relative excitonic emission at 425 nm (attributed to PNCs) is insensitive to oxygen in the low O$_2$ partial pressure range (0–20%), indicating that these PNCs are suitable for being used as the internal reference for gaseous O$_2$ partial pressure sensing (Figure 8b). As the O$_2$ fraction increases, Mn$^{1+}$ emission begins quenching and especially shows a high sensitivity to the low O$_2$ partial pressures (Figure 8c). Figure 8d shows the variation of Mn$^{1+}$ and excitonic PL intensity ratio ($I/I_0$) versus the O$_2$ percentage. The Mn$^{1+}$ PL intensity ratios ($I/I_0$) for O$_2$ partial pressures lower than 20% depict a linear relationship that follows the Stern–Volmer equation.

### Table 1. PLQY of Mn-doped PNC samples with different Mn/Pb ratios.

| Mn/Pb | PLQY [%] |
|-------|----------|
| 0     | 6 ± 2%   |
| 4/6   | 30 ± 2%  |
| 8/2   | 40 ± 1%  |
| 9/1   | 50 ± 1%  |
\[
\frac{I_0}{I} = K_{SV}[pO_2] + 1
\]

where \( I_0 \) and \( I \) represent the maximum \( Mn^{\text{I}2} \) PL intensities in the absence and presence of specific \( O_2 \) partial pressures (%), respectively, and \( K_{SV} \) is the Stern–Volmer constant. From the results shown in Figure 8d, \( K_{SV} = 0.02 \) \([pO_2]^{-1} \) \((R^2 = 0.97)\) for \( Mn^{\text{I}2} \) emission peak and \( K_{SV} = 0.0021 \) \([pO_2]^{-1}\) for excitonic emission.

As \( O_2 \) is a quencher of PL, this quenching is a convenient method for detecting this molecule. The properties and behavior of oxygen reflect its unique electronic structure. As shown in Figure 9, unlike many molecules, \( O_2 \) has a biradical electronic nature. Its ground state, \( O_2(X^3\Sigma_g^-) \), is a spin triplet and its highest-energy excited electronic states, \( O_2(a^1\Delta_g) \) and \( O_2(b^1\Sigma_g^+) \), are spin singlets. Therefore, triplet–triplet energy transfer between the \( O_2 \) and \( Mn \) triplet state is extremely efficient, so the phenomenon of PL quenching is described as a dynamic process of the collisional interaction of an \( O_2 \) molecule with the \( Mn \) : \( MaPb(Br/Cl)_3 \) NCs, where it temporarily deactivates the \( Mn \) emission. After collision, energy is transmitted to the \( O_2 \) molecule, resulting in its transfer from the ground state to its excited state.

The high density of electron transfer from perovskite singlet state to \( Mn^{\text{I}2} \) triplet state through ISC can usually increase the probability of triplet–triplet energy transfer between \( O_2 \) and \( Mn \) triplet-state. So, it can enhance the sensitivity of the sensor. It shows that the sensitivity of the sensor is related to the \( Mn \) PL intensity, which is determined by halide anions.

Figure 10 shows the response time of the \( O_2 \) partial pressure sensor which is measured by the reversibility of \( Mn^{\text{I}2} \) emission peak when the atmosphere is periodically switched from 100% \( N_2 \) to 100% \( O_2 \). The response time and the recovery time of the gas sensor which are the times measured to reach 90% of the maximum output and 10% of minimum output are 6 and 21 s, respectively.

Figure 11a–c shows the effect of temperature variation on the intensity and peak positions of the PL for both \( Mn^{\text{I}2} \) and excitonic emissions in the \( N_2 \) atmosphere. The redshift of excitonic and blueshift of \( Mn \) PL peaks are observed when the temperature rises in the range of 10–100 °C. For the excitonic emission of PNCs, the increased temperature leads to gradual PL quenching as a result of photon–phonon coupling and the
thermally activated trapping of charge carrier, and the redshift emission is also induced by thermal expansion of the crystalline lattice. [14] However, the Mn PL emission behaves oppositely, the emission peak blueshifts, and the PL intensity enhances. To explain the effect of temperature on the PL characteristics, the schematic of the band diagram for different temperatures is shown in Figure 11d. The PL intensity of Mn depends on spectral overlap between exciton-to-Mn energy-state transfer and defect density. With increasing temperature from 10 to 60°C, the bandgap decreases, leading to more spectral overlap between exciton-to-Mn energy; as a consequence, Mn PL intensity increases. Moreover, the spectral Mn\(^{+2}\) PL simultaneously blueshifts along with increasing temperature, resulting in the enhanced spectral overlap between exciton-to-Mn energy. For higher temperatures (>60°C), Mn PL quenching appears as a result of the thermally activated nonradiative trapping defects (deep-level trap state). Blueshift of the spectral Mn\(^{+2}\) PL can be attributed to the crystal thermal expansion. [14, 19] The observation of temperature-dependent exciton-to-Mn energy transfer in Mn-doped PNCs can be used for temperature sensing according to the linear ratiometric emission between perovskite and Mn.

Encouraged by the opposite behavior of Mn and excitonic PL intensity by temperature variation, a new highly sensitive ratiometric temperature sensor is developed. To determine the temperature effect on the output of the ratiometric sensor, the PL ratio (PLR) relation is defined by $PLR = \frac{I_{Mn}(T)}{I_{ex}(T)} / \frac{I_{Mn}(T_{ref})}{I_{ex}(T_{ref})}$, where $T_{ref} = 298 K$. Here, the intensities, $I_{Mn}$ and $I_{ex}$, represent the integrated PL emission for each corresponding peak.

Figure 10. a) Reversibility test under the alternating exposure to 100% O\(_2\) or 100% N\(_2\) (Mn\(^{+2}\) emission peak), excited by 405 nm laser. b) The response time curve for one cycle.

Figure 11. Sensing responses of the Mn:MaPb(Br/Cl)\(_3\) film to temperature excited by 405 nm laser. a–c) Mn and excitonic PL intensities as functions of temperature. d) Schematic illustration of the band diagram changes by temperature variation.
The measured values are depicted in Figure 12a fitted by

\[ \text{PLR} = Ae^B + C \]  

(2)

where \( A, B, \) and \( C \) which are related to Mn:MAPb(Br/Cl)3, are equal to \( 5.24 \times 10^{-12}, 7743, \) and 0.085, respectively, and \( T \) is the absolute temperature. To compare the sensitivity of this probe with the other ratiometric temperature sensors, we use the absolute sensitivity \( (S_a) \) and relative sensitivity \( (S_r) \) defined as

\[ S_a = \frac{d(\text{PLR})}{dT} = -Ae^B \times B \times T^2 = -5.24 \times 10^{-12}e^B \times 7743 \]  

(3)

\[ S_r = 100\% \times \frac{S_a}{Ae^B + C} \]  

(4)

Figure 12b shows the calculated values of \( S_a \) and \( S_r \) at different temperatures. The highest values of \( |S_a| \) and \( |S_r| \) are determined as 0.34 K\(^{-1}\) and 9.36% K\(^{-1}\) at 284.14 K, respectively.

In Table 2, the characteristics of the sensing probes fabricated in this work are compared with some other reported \( \text{O}_2 \) ratiometric PL probes based on NCs. As mentioned, in this work, NCs are synthesized in situ while in other works the colloidal method was used. Undesirably, the colloidal method needs a high-temperature condition; the synthesized NCs should be extracted and carefully purified for removing excess precursors and surfactants before being used as OSPs. However, the in situ strategy used in this work is a one-step process, benefiting this technology by lowering the cost and simplifying the fabrication process without needing any complex instruments. It provides the fabrication of sensing probes based on a dual-emission Mn:MAPb(Br/Cl)\(_3\) PNC layer with a high PLQY of 50%. The high PLQY leads to an enhanced signal-to-noise ratio and low-cost measuring equipment. On the other hand, our work which is based on the luminophore material of doped PNCs exhibits broader absorption spectra, long-term photostability, tunable emission, and larger Stokes shift as compared with the other dual-emission structures using two luminophore materials such as CsPbBr\(_3\) NCs/PtTFPP\(^{[2][b]}\) and BlueCy-TPB loaded PMMA-MA NPs/PtOEP\(^{[20]}\). The results reveal the high potential of the perovskite materials for being used as active layers of the sensors with the ability to tune the sensing properties by changing the perovskite composition as compared with the conventional gas sensors. As Casanova-Chafer et al. explained in their work\(^{[21]}\) by changing the perovskite composition, the selectivity of the sensor can be adjusted systematically.

Table 3 summarizes some of the important characteristics of the reported temperature ratiometric PL probes based on NCs and the results achieved in this work. As observed, the PLQY and \( S_r \) of the sensor fabricated in this work are the highest values ever recorded on dual-emission temperature ratiometric sensors.

### 3. Conclusion

In summary, a simple in situ method was used to synthesize dual-emission Mn:MAPb(Br/Cl)\(_3\) PNC films. In this method, polymer chains were utilized to control the size of the PNCs and passivate their boundary defects. Also, using this method, the simple addition of Mn impurities into the perovskite layer was provided, leading to the formation of bright dual-emission Mn:MAPb(Br/Cl)\(_3\) PNC film with optimum ratios of Mn/Pb = 1/9 and PbBr\(_2\)/(PbBr\(_2\)+PbCl\(_2\)) = 2/10. As a result of the Pb substitution by Mn and the boundary defect passivation by PVP, PNCs with a PLQY as high as 50 were achieved. The

| Probe | Response signal | Synthesis method | PLQY (%) | \( \text{O}_2 \) Sensitivity (100) | Ref. |
|-------|-----------------|------------------|----------|-------------------------------|-----|
| Mn:MAPb(Cl/Br)\(_3\) | Mn\(^{2+}\) dopants | In situ | 50 | 1.55 | This work |
| Mn:CsPbCl\(_3\) | Mn\(^{2+}\) dopants | Colloidal | 37 | 2.13 | [9] |
| CsPbBr\(_3\) NCS/PtTFPP | Dye:PtTFPP | Colloidal | Not mentioned | 3.5 | [5] |
| BlueCy-TPB-loaded PMMA-MA NPs/PtOEP | Dye:PtOEP | Colloidal | 35 | 3.8 | [20] |
Table 3. A comparison of the performance of our probe with some other reported temperature ratiometric probes based on dual emission.

| Probe | Response signal | PLQY [%] | $S_r$ | Detection range [K] | Ref. |
|-------|-----------------|---------|------|---------------------|------|
| Mn:MAPb(Cl/Br)$_3$ | Mn$^{2+}$ dopants | 50 | 9.36 [% K$^{-1}$] | 284–320 | This work |
| Ag&Mn:ZnInS | Mn$^{2+}$ dopants | 20% | 0.227 [% C$^{-1}$] | 274–354 | [23] |
| Mn:Li$_2$Zn$_3$Al$_5$Ge$_9$O$_{36}$ | Mn$^{2+}$ dopants | Not mentioned | 8.489 [% K$^{-1}$] | 304–374 | [24] |
| Eu$^{3+}$:Y$_2$O$_3$ | Eu$^{3+}$ dopants | Not mentioned | 3.93 [% K$^{-1}$] | 150–300 | [25] |

dual-emission thin film of PNCs was used as the sensing layer of the internal referencing ratiometric PL probes that detected O$_2$ gas partial pressure and ambient temperature simultaneously. As revealed, the excitonic and Mn emissions of Mn:MAPb(Br/Cl)$_3$ thin film showed different sensitivity to the change of temperature and O$_2$ gas partial pressure. As the excitonic PL was insensitive to the O$_2$ partial pressures (0–20%), while, the Mn PL presented a high sensitivity to gas partial pressures, the excitonic PL was considered as the internal reference. For temperature-sensing properties both PL peaks showed opposite behavior in the range of 284–340 K. Internal referencing ratiometric PL probes with the O$_2$ gas sensitivity of 1.55 and temperature sensitivity of 9.36% K$^{-1}$ were fabricated successfully, providing the simultaneous detection of temperature and O$_2$ gas concentration.

4. Experimental Section

Synthesis of Methylammonium Chloride: First, 13.5 mL of methylamine solution (CH$_3$NH$_2$, Sigma-Aldrich, 98%) (40 wt% in aqueous solution) was poured into a balloon and placed in a container filled with ice to control the temperature during the synthesis at 0°C. While the solution was stirred on a magnetic stirrer, 22 mL of hydrobromic acid (HCl, Sigma-Aldrich, 57 wt% in water) was added dropwise. After stirring for 2 h, the synthesized powder was precipitated using diethyl ether ([CH$_3$CH$_2$]$_2$O, Mojalali) as an antisolvent. The white powder was purified by dissolving in methanol and then precipitated by adding diethyl ether three times. Finally, the powder was dried in a rotary evaporator at 60°C for 1 h.

Synthesis of Mn-Doped PNCs: To synthesize Mn:MAPb(Cl/Br)$_3$ PNCs, PbBr$_2$ (Sigma-Aldrich, 99.999%), polyvinylpyrrolidone (PVP, Sigma-Aldrich), and MnCl$_2$ (Sigma-Aldrich, 98%) were separately dissolved in anhydrous dimethylformamide (DMF, Sigma-Aldrich) at 1 M concentration and then stirred at 90°C for 1 h. In addition, CH$_3$NH$_2$Cl and PbCl$_2$ (Sigma-Aldrich, 99.999%) were separately dissolved in anhydrous dimethyl sulfoxide (DMSO, Sigma-Aldrich) at 1 M concentration and then stirred at 90°C for 1 h. Mn-doped PNCs were prepared by adding different amounts of MnCl$_2$ to PbBr$_2$ + PbCl$_2$ solution and PbBr$_2$ to PbBr$_2$ + PbCl$_2$ solution where the precursors’ ratios were engineered to achieve a high PLQY and high sensing performance for the PNCs.

To control the size of the PNCs, different concentrations of PVP were added to the perovskite precursor solution. The PNC layers were synthesized by pouring 60 μL of precursor solutions on cleaned, dried, and preheated glass substrates at 90°C and subsequently spin coated at 3000 rpm for 40 s. After deposition, the substrate was quickly transferred to the hot plate and annealed for 10 min at 130°C to complete the crystal formation and remove the residual solvents under ambient atmosphere.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

dual emissions, O$_2$ sensitive probes, quenching, ratiometric and internal referencing

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