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Stable fluorescent NH₃ sensor based on MAPbBr₃ encapsulated by tetrabutylammonium cations



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ABSTRACT

Recently, organic-inorganic halide perovskite materials were investigated on gas sensing due to their excellent optical properties and gas sensitivities. Here, we designed a stable fluorescent perovskite-based sensor for NH₃ detection, in which the CH₃NH₃PbBr₃ (MAPbBr₃) film was deposited on the GeO₂ substrate and also capped by tetrabutylammonium (TBA) ligand as a stabilizing agent. This as-fabricated MAPbBr₃-TBA-based sensor exhibited the relatively strong and stable photoluminescence (PL) intensity, thereby expanding the fluorescence response range for NH₃ sensing. Upon exposure to NH₃ gas, the PL intensity quenched rapidly by 62.5% with short response time (61 s) and recovery time (65 s). The sensor also possessed a linear relationship between the PL intensity and concentration of NH₃ in the range of 0–100 ppm, and presented excellent reversibility, higgs selectivity, and humidity stability. Furthermore, the NH₃ sensing mechanism was investigated based on X-ray diffraction (XRD), Fouriertransform infrared spectroscopy (FT-IR), Differential thermal analysis-Thermogravimetry (DTA-TG) and fluorescence lifetime measurements, in which the NH₃ molecules might permeate the capped TBA ligand and then induce structure transformation of inner MAPbBr₃ crystal. This study indicated that the asprepared MAPbBr₃-TBA-based sensor might provide promising applications on NH₃ gas detection.

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1. Introduction

As a raw material, ammonia (NH₃) is extensively utilized in the fields of agriculture and chemistry industries. However, NH₃ as toxic gas can cause serious harm to the human body, even at quite low concentration. Generally, human tolerance levels of NH₃ gas were defined at 15 min exposure limit of 35 ppm and an 8 h exposure limit of 25 ppm [1,2]. So it is necessary to adopt effective methods to monitor NH₃ gas precisely. In this regard, researchers have proposed many novel detection techniques based on various sensing materials, such as metal oxides [3–5], conducting polymers [6–8] and quantum dots [1]. Most of them can be classified as electrical-type and optical-type sensors, mainly depending on the changes in electrical or optical signals induced by NH₃ gas.

For the metal oxide-based sensors, many available sensing materials were developed including ZnO, In₂O₃, SnO₂, SnS₂, MoO₃, WO₃

* Corresponding author. E-mail address: cbjing@ee.ecnu.edu.cn (C. Jing). and TiO₂ [9,10]. For example, Chen et al. reported an NH₃ sensor based on the SnO₂-nanorods/reduced graphene oxide composites with fast response time (8 s) and recovery time (13 s) at 200 ppm NH₃ [3]. Recently, Maity et al. designed a novel and wearable NH₃ sensor by combining the polyaniline and multiwall carbon nanotubes based on strong Π - Π interaction between them [11]. Despite these significant developments, it is still challenge to achieve superior sensors with high stability and sensitivity.

In the last decades, metal halide perovskites have drawn much attention due to their excellent optical and electrical properties. Thus, the perovskites were widely investigated in several fields such as solar cells [12], light-emitting diodes [13], photo-detectors [14] and lasers [15]. Besides, the perovskites can be also applied as the sensors to detecting NO₂ [16], O₂ [17], O₃ [18], NH₃ [19–24], SO₂ [25], humidity [26], temperature [27], organic vapors [28,29] and metal ions [30]. For the NH₃ gas sensing, it was firstly reported by Zhu et al. that the NH₃ molecules were able to react with the CH₃NH₃PbI₃ (MAPbI₃), followed by the color changing from brown to colorless [22]. To enhance the sensitivity and stability, Ruan et al.





designed and fabricated a fiber probe based on MAPbX₃ (X = Cl, Br or I) single crystals [21]. In their case, the recorded photoluminescence (PL) decreased dramatically by 60%, upon exposure to NH₃ vapor. However, the fabrication of this sensor may require a complex single-crystal growth process, and the accurate NH₃ concentration was not mentioned. Herein, it is an urgent need to develop simple and facile perovskite sensors to detect the low concentration NH₃ with long-term stability.

Recently, a long alkyl chain salt tetrabutylammonium-bromide (TBA) was used as a passivation agent to stabilize the perovskite, owing to the ability to control crystallization [31]. For the sensing application, we expected that this capping layer on the surface of perovskite could increase its stability with suitable gas permeability. In order to explore this possibility, in this paper, we prepared the TBA-coated MAPbBr₃ films on GeO₂ substrates to investigate the influences of TBA on NH₃ sensing. The pre-deposited GeO₂ substrates possessed the rough surface which facilitated the adhesion and dispersion of perovskite crystals compared to the smooth glasses. The sensing performance of the as-prepared MAPbBr₃-TBAbased sensor was determined that the PL intensity quenched rapidly upon exposure to NH₃ gas and then recovered to the initial PL intensity after removing NH₃ gas. The NH₃ sensing mechanism was also studied based on XRD, FT-IR, DTA-TG and PL lifetime measurements. Hence, it paves the way for the application of organicinorganic halide perovskite on NH3 detection.

2. Experimental

2.1. Preparation of GeO₂ substrates

The growth of GeO₂ layers was taken by a modified liquid phase deposition method which reported by Jing et al., previously [32]. In detail, 0.75 mL of aqueous ammonia (26–28 wt%) was dissolved in deionized water (25 mL) at 65 °C, followed by adding 1.5 g GeO₂ powders. After stirring for 30 min, the transparent solution was obtained. Then, the nitric acid (36 wt%) was added dropwise to the above solution until the pH was adjusted to the value of 2. Afterward, the glass sheets (10*10*1 mm³), sonicated successively in acetone and ethanol for 20 min, were soaked into the above aqueous solution. The deposition process was carried out for 36 h at room temperature. Finally, the white GeO₂ layers were observed on the glass sheets, and then these GeO₂ substrates were washed by deionized water and ethanol, followed by drying at 100 °C for 1 h.

2.2. Synthesis of CH₃NH₃Br

CH₃NH₃Br (MABr) was synthesized by mixing methylamine (MA, 30 wt% in ethanol) with equimolar amounts of aqueous HBr (40 wt% in water). First, the MA in anhydrous ethanol was stirred and cooled to 0 °C by adding HBr acid slowly. Subsequently, the reaction solution was stirred continuously for 2 h under N₂ atmosphere and then evaporated by rotary evaporation at 50 °C. The asobtained MABr precipitate was washed with diethyl ether several times to remove the residual HBr and then dried at 60 °C in a vacuum oven overnight.

2.3. Preparation of perovskite films

Initially, the MAPbBr₃ (0.3 M) precursor solution was prepared by dissolving equimolar amounts of MABr (67.2 mg) and PbBr₂ (220 mg) in N, N-Dimethylformamide (DMF, 2 mL) under vigorous stirring. Then, the above solution was divided into 2 equal parts. The TBA raw material (19.3 mg) was added in one part of them with the ratio of TBA/MA at 20%. All the solutions were stirred at 50 °C overnight. For the perovskite film deposition, one droplet (40 μ L) of the perovskite precursor solutions with/without TBA were spincoated on GeO₂ substrates at 2000 rpm for 60 s Meanwhile, to induce the crystallization quickly, 100 μ L toluene was dropped onto the substrates at 10 s during the spinning process. Finally, the asprepared samples were annealed at 60 °C for 10 h.

2.4. Characterizations

The film morphologies and element distributions were observed by using a scanning electron microscope combined with an energydispersive X-ray spectroscope (SEM/EDS, Gemini 450). X-ray diffraction patterns were measured by a rotating Cu K α anode X-ray diffractometer (XRD, Rigaku Ultima IV) under 35 kV and 20 mA. The scanning range was set as $5^{\circ} < 2\theta < 50^{\circ}$ with a speed of 10° min⁻¹. The infrared spectrum was recorded on a Bruker 80 V Fourier Transform Infrared Spectrometer (FT-IR). The PL spectra data of samples were collected using the fluorescence spectrophotometer with a slit width of 2 nm (LengGuang, F97pro). The thermal behaviors were measured by differential thermal analysis (DTA) and thermogravimetry (TG) using a Mettler Toledo TGA/SDTA 851^e system; measurements were carried out from 25 to 700 °C (heating rate: 10 °C/min) under N₂ flow. Finally, the PL decay lifetimes were measured by an Edinburgh Instruments FLS920 fluorescence spectrometer equipped with a picosecond pulsed diode laser ($\lambda = 371.6$ nm, pulse width = 66.3 ps) and a time-correlated single-photon counting unit.

2.5. Fabrication of NH₃ gas sensors

The schematic measurement setup is shown in Fig. 1. The quartz cuvette (10*10*40 mm³) was used as a gas chamber to hold perovskite samples. The PL spectra of samples were excited by a Xe lamp source and then recorded by a photomultiplier tube (PMT) detector. Different concentrations of NH₃ gas were obtained via mixing appropriate pure N₂ and NH₃ gases. The target gas was blown into the chamber by gas sampling pump with a constant flow rate of 0.5 L/min. The gas response was determined by calculating the value of response $(I_0 - I)/I_0 \times 100\%$, where the I_0 was the initial PL intensity under NH₃-free condition, and I was the PL intensity in the present of NH_3 gas. The response time T_{res} was defined as the time for the sensor to reach 90% of maximum PL intensity change upon exposure to NH₃ gas, and the recovery time T_{rec} as the time to recover 90% of maximum PL intensity change after removing NH₃ followed by exposure of pure N₂ gas. To measure the effect of ambient moisture on the response of this gas sensor, we carried out the PL measurement under different relative humidity (RH) conditions (using the vapors of saturated salt solutions including MgCl₂, K₂CO₃, NaBr, NaCl, KCl and K₂SO₄ at room temperature).

3. Results and discussion

Fig. 2 presents the SEM images and EDS maps of the as-prepared perovskites deposited on glass or GeO₂ substrates. It can be seen that the perovskite MAPbBr₃-TBA possesses the piece-like shape adhered to a smooth glass substrate (Fig. 2a), while the morphologies of MAPbBr₃ and MAPbBr₃-TBA on GeO₂ layers show the typical perovskite grains (Fig. 2b and c). It is reasonable that the GeO₂ layer has a rough surface (Fig. 2b), which may facilitate the heterogeneous nucleation and dispersion of perovskite crystals, compared to the smooth glass substrate. Clearly, it appears the cubic-structure grains in the MAPbBr₃-TBA sample (Fig. 2d), in which the grain sizes are smaller than that of MAPbBr₃ (Fig. 2c), indicating the TBA ligand may modify the outer surface perovskite crystal to reduce grain size [31]. In order to verify whether these cubic grains are MAPbBr₃-TBA, we selected some grains (the rectangular area in Fig. 2d) and measured the elemental composition



Fig. 1. Schematic diagram of experimental setup for NH₃ sensing.

by EDS, as shown in Fig. 2f-j. The result indicates the presence of C (43.7 at%), N (11.2 at%), Pb (13.0 at%) and Br (32.2 at%), which is closed to the experimental compositions. Fig. 2e shows the cross-sectional image of MAPbBr₃-TBA/GeO₂ substrate with the thickness at about 10 μ m. It is worth noting that the layers of both GeO₂ and perovskite are difficult to distinguish because the perovskite film is too thin and several grains are embedded into the gap of the GeO₂ layer (see EDS data in Fig. S1).

Fig. 3a gives the XRD patterns of MAPbBr₃ and MAPbBr₃-TBA films. In these two samples, it appears two prominent diffraction peaks at 15.2° and 30.4°, identified with the (100) and (200) planes of MAPbBr₃ crystal structure, respectively [33]. In the MAPbBr₃-TBA sample, the peak at low angle 7.6° is also observed, assigned to the dimensional 2D perovskite phase [31,34]. Since the large size cation TBA⁺ is difficult to insert into 3D MAPbBr₃ crystal, it may grow on the surface of perovskite as a capping layer [35,36]. Interestingly, the main diffraction peaks (15.2°) appear slight right-shift and become broaden upon the addition of TBA⁺ cations (see Fig. S2), indicating the reduction in grain size of the 3D perovskite, which is consistent with the SEM data. This case also demonstrates that the TBA ions would form a passivation layer on the surface of perovskite to limit the growth of perovskite rather than insert into the inner of 3D crystal. FT-IR spectra were also conducted to verify the presence of TBA in perovskite, as shown in Fig. 3b. The broadband peak at 3450-3300 cm⁻¹ is observed in two samples, mainly assigned to the N–H stretching of amine salts and the OH- stretching of incidental water vapor. In addition, the vibration peak at 2960 cm⁻¹ can be assigned to the CH- stretching characteristic of both TBA⁺ and MA⁺ cations, while the peak at 2865 cm⁻¹ corresponds to the $-CH_2$ - group of only TBA⁺ cations [37]. The above results indicate the presence of TBA⁺ and MA⁺ cations in the MAPbBr₃-TBA sample.

To study the effect of the substrate and TBA on optical prosperities of perovskite films, Fig. 4 gives the PL spectra of perovskite samples including the MAPbBr₃-TBA on glass, MAPbBr₃ on GeO₂ and MAPbBr₃-TBA on GeO₂. In these three samples, MAPbBr₃-TBA on GeO₂ presents the maximum PL intensity. It implies that the GeO₂ layer may provide a good crystal growth substrate for perovskite and the TBA ligand could passivate the surface defects and grain boundaries of perovskite crystal by interacting with Pb atoms, thereby inhibiting the non-radiative recombination [35,38]. Moreover, a slight red-shift of the peak appears in the TBA-doped sample. We infer that the TBA ligand attached to perovskite surface may form several intermediate energy levels, contributing to the tiny reduction in energy bandgap. This red-shift phenomenon is similar to that of TBA-doped CsPbBr₃ perovskite which reported



Fig. 2. SEM image of (a) MAPbBr₃-TBA on smooth glass substrate, (b) GeO₂ layer, (c) MAPbBr₃ on GeO₂ substrate, (d) MAPbBr₃-TBA on GeO₂ substrate. (e) cross-sectional image of MAPbBr₃-TBA/GeO₂ substrate. (f, g, h, i) EDS maps of (d) rectangular area for C, N, Pb, and Br, respectively. (f) Elemental microanalysis.



Fig. 3. XRD patterns (a) and FT-IR transmission spectra (b) of MAPbBr₃ and MAPbBr₃-TBA films.

previously by Song and co-authors [35]. Nevertheless, in several other studies, the blue-shift characteristic was found upon loading the long-chain amine salts, attributed to the reduced 3D perovskite structure dimensionality [38,39]. In contrast, the main roles of TBA dopant in this work may be utilized to modify and passivate surface grain boundaries and defects.

To investigate the photo-stability of as-prepared samples, we measured the PL intensity of perovskites as a function of time (see Fig. S3). There is no significant decrease of the PL intensity in perovskite MAPbBr₃-TBA, while the PL intensity in pristine MAPbBr₃ drops by 10% within 300 s. The result indicates the TBA layer can keep the perovskite more stable to light irradiation. Actually, this is an important prerequisite for fluorescent sensors.

As previously reported, long-chain alkyl ammonium cations were reacted with PbBr₂ and only fitted the periphery of the PbX₆ octahedra with their chains dangling [40]. Thus, at a low doping concentration of TBA, the perovskite crystal surface is not completely covered by TBA⁺ cations, which gives NH₃ molecules a chance to enter the interior. Also, Nazzal et al. reported the surface passivation layer could be permeable to gases with the help of the photo-activation of vibration modes of the crystal lattice induced by photon-phonon coupling [41].

In order to investigate the response of the perovskite sensor towards NH_3 gas, we measured the color changes in fluorescence before and after the exposure of NH_3 under ultraviolet (UV) light, as shown in Fig. 5. It can be observed that the significant quenching of fluorescence occurs when blowing NH_3 .

Fig. 6a presents the response transients of MAPbBr₃-based and MAPbBr₃-TBA-based sensors to 100 ppm NH₃ gas under 365 nm illumination. Upon exposure to NH₃, the pristine MAPbBr₃ shows the maximal PL quenching of 74.4%, while the MAPbBr₃-TBA shows the value of 62.5% within ~90 s. It seems that the TBA passivation layer causes a negative impact on NH₃ detecting. However, this negative impact could be negligible, because the PL intensity is able to recover fully within a short time after the removal of NH₃ gas. The response and recovery times are calculated as 61 s and 65 s, respectively. In addition, it should be noted that neither of these sensors reaches the entire PL quenching. It suggests that the NH₃ molecules may be limited to interact with the near-surface region of perovskite inducing the surface defects. Actually, in case of immersing into high-pressure NH₃ gas, the NH₃ molecules could not only contact with the surface of perovskite, but also penetrate deeply into the bulk [42,43].

To investigate the reproducibility of the as-prepared sensor, Fig. 6b gives the reversible response of the MAPbBr₃-TBA-based sensor versus the time under constant concentration NH₃ gas (100 ppm). The PL intensity quenches rapidly upon exposure to NH₃ gas, afterward, it recovers to the initial level when removing NH₃. This excellent reversibility to NH₃ paves a way for the practical application of a gas sensing system. In addition, we find that different response and recovery times are illustrated during these cycles, probably resulting from the changes in gas flow or the microstructure state of perovskite after reacting with NH₃. Further study is underway.



Fig. 4. PL spectra of MAPbBr $_3$ and MAPbBr $_3$ -TBA films on glass or GeO $_2$ substrates, upon excitation of 365 nm.

To explore the sensitivity of the perovskite sensor towards NH_3 gas, we recorded the PL response under different concentrations of NH_3 gas (see Fig. 7a). As the NH_3 concentration increases, the PL



Fig. 5. Photographs of fluorescence changes in $MAPbBr_3$ -TBA film before and after NH_3 treatment, under UV light.



Fig. 6. (a) The response transients of MAPbBr₃-based and MAPbBr₃-TBA-based sensors to 100 ppm NH₃ gas. (b) Reproducibility of MAPbBr₃-TBA-based sensor when switching between N₂ and NH₃ gas, alternately.

intensity of the sensor decreases proportionally. From Fig. 7b, an excellent linear relationship is exhibited between the PL intensity and concentration of NH₃ in the range of 0–100 ppm. The slope is 18.7 with R² of 0.977. The limit of detection (LOD) is calculated by an equation as $LOD = 3\sigma/S$, where σ is the relative standard deviation and *S* is the slope of the calibration curve. On the basis of this equation, the LOD for this sensor is calculated to be 0.46 ppm. It worth noting that the PL peak appears a slight blue-shift when exposure to excess NH₃ gas (see Fig. S4), implying the NH₃-induced structure transformation of perovskite [22].

Previously, it was reported that the humidity had a negative effect on perovskite solar cells, as the phase transformation of perovskite can take place upon exposure to water vapor [17,44]. To verify the effect of humidity on perovskite sensors, we carried out the humidity measurement of perovskite sensors under different RH condition (see Fig. 8a). For the MAPbBr₃ and MAPbBr₃-TBA perovskite sensors, the PL quenching appears upon exposure to 98% RH water vapor, in which the extent of PL decline was 22.1% and 13.9%, respectively. Expectantly, for the MAPbBr₃-TBA-based sensor, the PL can be restored absolutely after removing water vapor, attributed to the protective effect of the TBA passivation layer. As can be seen in the insert of Fig. 8a, the maximum values of PL quenching are determined under different RH environment, indicating that the water vapor has little effect on the performance of MAPbBr₃-TBAbased sensor.

The selectivity performance is also one of important parameters to NH₃ sensor. So we measured the response of MAPbBr₃-TBAbased sensor toward various saturated organic vapors, including ethanol, acetone, cyclohexane, toluene and chlorobenzene vapors (see Fig. 8b). It can be observed that this sensor displays an excellent specificity toward NH₃ (100 ppm) in comparison with other saturated organic vapors. Interestingly, the enhanced PL response occurs upon exposure to ethanol or acetone vapor. It may be due to that the ethanol and acetone act as vacancy filler, increasing the electron-hole recombination in perovskite [45].

To explore the NH₃ sensing mechanism, we investigated the structure and composition changes in perovskite before and after excess NH₃ treatment. Beforehand, the MAPbBr₃-TBA sample was treated in a high concentration NH₃ atmosphere for several hours. At this time, the fluorescence became weak and took a long time to recover after removing NH₃ gas.

Fig. 9a depicts the XRD patterns of MAPbBr₃-TBA samples before and after excess NH₃ treatment. After NH₃ treatment, several prominent diffraction peaks of MAPbBr₃ crystal become weak even disappeared such as (100) and (200), whereas the low angle at 7.7° (2D phase) is almost unchanged. Moreover, the diffraction peaks of (110) and (200) appear right-shift, indicating the size decrease of crystal, mainly due to the decomposition of MAPbBr₃. These results imply that the NH₃ molecules might tend to react with the inner MAPbBr₃ rather than outside 2D TBA capping layer, leading to the phase transformation of MAPbBr₃ [21].

FT-IR spectra were also used to evaluate the changes in compositions of the MAPbBr₃-TBA sample, as shown in Fig. 9b. There is no obvious change in 2960 cm⁻¹ and 2865 cm⁻¹ peaks before and after NH₃ treatment. The result suggests that no significant loss of MA and TBA after NH₃ treatment. Previously, Huang et al. reported the MA gas could evaporate from perovskite upon exposure to NH₃, owing to that the CH₃NH₃⁺ cations would be replaced by the NH₄⁺ cations (NH₃ + CH₃NH₃⁺ \rightarrow NH₄⁺ + CH₃NH₂ \uparrow) [42]. In the MAPbBr₃-TBA sample treated by NH₃, we speculate that the generated MA gas molecules may still remain in the perovskite. These MA molecules may locate in uncoordinated states to form the specific intermediate phase or adhere to the TBA layer by van der Waals force [21,46].

Furthermore, to elucidate the sensing mechanism from thermal decomposition behavior, we carried out the DTA-TG measurements



Fig. 7. MAPbBr₃-TBA-based gas sensor. (a) The PL quenching toward different concentration of gaseous NH₃ (0–100 ppm), (b) the plot of PL intensity versus concentration of NH₃.



Fig. 8. (a) The humidity response transients of the MAPbBr₃-based and MAPbBr₃-TBA-based sensors under 98% RH condition, the insert shows the PL quenching in MAPbBr₃-TBA sample under different RH condition. (b) The selectivity of MAPbBr₃-TBA-based sensor to various saturated organic vapors at room temperature (25°C).



Fig. 9. XRD patterns (a) and FT-IR transmission spectra (b) of MAPbBr₃-TBA samples before and after high concentration NH₃ treatment.

on MAPbBr₃-TBA (see Fig. S5). In the 1st derivative curve of reference MAPbBr₃-TBA sample (see Fig. S5a), three weight loss peaks are located at 318, 372 and 643 °C, ascribed to the loss of TBA⁺,

MA⁺, and inorganic PbBr₂, respectively [47,48]. For the NH₃ treated MAPbBr₃-TBA (see Fig. S5b), a weak loss peak at 147 $^{\circ}$ C can be observed, which may be attributed to the uncoordinated MA [21].



Fig. 10. Schematic diagram of NH₃ sensing mechanism for MAPbBr₃-TBA-based sensor.

Moreover, the weight loss at 372 $^{\circ}$ C becomes weak, indicating the reduction of protonated MA⁺ content in perovskite. It is suggested that the thermal stability of perovskite decreases upon exposure to NH₃, which could be one of the evidences that the NH₃-induced decomposition of perovskite.

In addition, we measured the time-resolved PL to further understand the sensing mechanism (see Fig. S6). The MAPbBr₃-TBA sample presents a long PL lifetime at 57.65 ns, while it decreases to the 27.52 ns after NH₃ treatment, indicating the increase of defect. It may be caused by perovskite decomposition, leading to the nonradiative recombination.

To shed light on the NH₃ sensing mechanism, Fig. 10 depicts the schematic diagram of reversible NH₃ sensing processes. It can be considered as the cation exchange mechanism [42]. Under the excitation of ultraviolet (UV) light, the strong PL spectrum is emitted from the MAPbBr₃-TBA perovskite sample. Initially, the NH₃ molecules would permeate the capped TBA ligand due to the small molecular size of NH₃ and photon-phonon coupling [41] and then induce the decomposition and structure transformation of MAPbBr₃ crystal. This process will bring about the formation of NH4PbBr3 and MA, leading to the PL quenching [21]. Based on the above characterization measurements and analysis, we speculate that the gaseous MA might interact with NH₄PbBr₃ to form the intermediate phase NH₄PbBr₃·MA rather than sublimating from inside [21,49]. Meanwhile, the outside TBA ligands with large steric hindrance would also retard the MA sublimation. After the removal of NH₃, the chemical conversion of $NH_4^+ + CH_3NH_2 \rightarrow NH_3 + CH_3NH_3^+$ occurs via a transition state of $H_3N \cdot H \cdot CH_2NH_2$ [46]. Consequently, the primary perovskite is restored gradually and then emerging the initial strong PL signal.

4. Conclusions

In summary, a novel NH₃ sensor has been developed by using the TBA-capped MAPbBr₃ film on the GeO₂ substrate. The TBA ligand could passivate the surface defects and grain boundaries of perovskite in which leading to the strong PL emission. For the MAPbBr₃-TBA-based gas sensor, upon exposure to 100 ppm NH₃ gas, the PL intensity rapidly decreases by 62.5% with short response time (61 s) and recovery time (65 s). Furthermore, this as-prepared sensor possesses an excellent linear relationship between the PL intensity and concentration of NH₃ in the range of 0–100 ppm with the detection limit of 0.46 ppm. According to the XRD, FT-IR, DTA-TG and PL lifetime measurements, the NH₃ sensing mechanism is speculated that the NH₃ molecules would permeate the capped TBA ligand and then induce the decomposition and structure transformation of MAPbBr₃. On the basis of these considerations, the MAPbBr₃-TBA-based perovskite sensor could pave the way for practical NH₃ gas detection.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Guishun Li: Conceptualization, Investigation, Methodology, Writing - original draft. Wenqian Zhang: Validation, Data curation. Changkun She: Formal analysis, Visualization. Shicheng Jia: Formal analysis, Visualization. Shaohua Liu: Project administration, Resources. Fangyu Yue: Supervision, Resources. Chengbin Jing: Funding acquisition, Supervision, Writing - review & editing. Ya Cheng: Supervision, Resources. Junhao Chu: Resources, Writing - review & editing.

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Appendix A. Supplementary data

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