Visual Colorimetric Detection of Pollutant Ammonia Gas using Family of Lead Halide Perovskites based Paper Sensors

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Abstract:

In this chapter, we show paper based ammonia sensors can be fabricated by simple wet route chemistry using family of perovskite lead halides, namely methyl ammonium lead iodide (MAPI), methyl ammonium lead bromide (MAPB), Formamidium lead iodide (FAPI). The paper sensors are capable of detecting ammonia gas by simple color change effect. Their response is qualitatively independent of cation and anion substitution. The sensor has very fast response (~10 sec for 10 ppm ammonia using MAPI) as well as good shelf life. Being grown on paper; the sensors are flexible, as well as disposable; also simple solution growth technique makes fabrication process of paper sensor cost effective. Thus the paper sensor could be employed as low cost, portable sensor for rapid and selective detection of atmospheric ammonia as well as a new application of lead halide perovskites beyond photovoltaic. The core mechanism of color change is conversion to its corresponding lead halides that has been established by several experimental tools.

Keywords: Paper Sensor, family of lead halide perovskites, Color Change, Wet route Chemistry, Ammonia

1. Introduction:

Realization of thin film gas sensors for efficient and cost-effective detection of toxic gases has gain considerable current interest due to its widespread applications from detection of environmental pollutants to non invasive point of care diagnosis[1-2].

One of the most hazardous environmental pollutants in the atmosphere is ammonia (NH_3). Detection of the presence of NH_3 at a low level is most desirable as the presence of the gas can occur in several areas like refrigeration, food processing and storage, fertilizers,

environmental protection, chemical technology, ammonification by nitrogen cycle etc. Generally, an acceptable level of NH_3 gas is 8-h exposure limit at 25 ppm and a short-term (15 min) exposure level at 35 ppm [3-4]. Sustained exposure may cause severe problem on human health. It can even be fatal if the inhaled gas has NH_3 above an acceptable limit of 500 ppm for 30 minutes. Brief exposure to concentrations above 1,500 ppm can cause pulmonary edema, a potentially fatal accumulation of fluid in the lungs [5].

Most of the reports available on thin film based gas sensors are electrical signal based and would need a peripheral arrangement for detection of the gas [6,7]. It is envisaged that if a color change sensor can be made where a visual detection can detect the hazardous gas in ppm level that would make it extremely easy to use as well as cost effective as it would need no electronics peripheral as well as need of trained operator can be obliterated. As examples, color change sensors based on papers are widely used for pH measurements as well as for measurements of glucose level in urine [8]. However, such easy to use sensors are not available for hazardous gases till date.

It is thus envisaged that development of a practical low cost, visual gas sensor (like a paper) for rapid and selective detection of atmospheric NH_3 gas in open as well as closed environment will be of great importance as personnel working in these areas can quickly detect even low level ammonia.

In last few years perovskite halides has emerged as an excellent candidate for room temperature ammonia gas sensor apart from its benchmark applications in photovoltaic & optoelectronics [9-11].

In this chapter, we show cheap paper based visual gas sensors can be made by family of lead based perovskite halide for easy and rapid detection of ammonia working at ambient temperature irrespective of physical and chemical differences. The $MAPbBr_3$ (MAPB) has cubic structure; $MAPbI_3$ (MAPI) has a tetragonal crystal structure whereas $FAPbI_3$ (FAPI) has trigonal structure with electronic band gap of 1.6eV, 1.52 eV and 2.3 eV respectively [12]. But the qualitative nature of sensing towards NH_3 remains the same for all three perovskites irrespective of crystal and electronic structure and cation, anion substitution. All the three lead based perovskites change their color in presence of NH_3 gas.

The important notion of this chapter is to establish the capability of the lead based perovskite halide family towards NH_3 gas sensing and to develop them as a common platform for possible next generation solid state room temperature NH_3 gas sensor with cost effective, easy, disposable, paper based technology.

2. Gas Sensor Fundamentals:

In a very simple and native way of speaking, a gas sensor is composed of a receptor and a transducer. The receptor is generally provided by a material and compositions of materials which changes its physical and /or chemical properties (dielectric constant, work function, mass etc) or emits light or heat upon interaction with the target gas. A transducer is a device which used to transform such an effect into an electrical signal. In a typical semiconductor gas sensor is generally, the material is used as receptor and sometimes acts as both receptor and transducer. However the overall components of a gas sensor, and the fabrication we will discuss in subsequent section [13]. The schematic of the typical gas sensor is shown in the following.

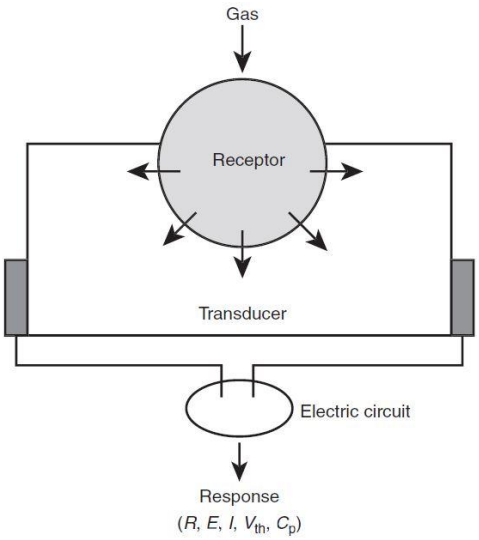

Figure 1: *Basic principle of gas sensor; gas sensor in a nut shell [13]*

3. Classification of Gas Sensor:

Solid-state gas sensors are generally operated on basic of the interaction between gas particles with surfaces and adjacent volumes. Different physical parameters, commonly,

resistivity, electrochemical potential, the density, and/or the optical properties are altered upon gas exposure.

To classify the gas sensor, several approaches can be used according operations on diverse principles. Taking into transducer mechanism, gas sensors are classified into several categories. The following table summarizes the different classes of gas sensor and their operating principles.

Sl No	Class of Gas Sensors	Operating Principles & Measured Quantities
1	Electrochemical (chemiristor)	Change in Voltage , Current , Capacitance/Impedance • Voltametry • Potentiomentry
2	Electrical	• Metal Oxide Conductivity • Electrolyte Conductivity • Work Function
3	Mass Sensitive	Change in the weight, amplitude, phase, frequency • Quartz Crystal Microbalance • Surface Acoustic Wave Propagation • Cantilever
4	Magnetic	Change in paramagnetic gas properties
5	Optical	Change in light Intensity, Color or Emission Spectra • Absorbance • Reflectance • Refractive Index • Light Scattering
6	Thermometric	Change in temperature, heat flow, heat content • Thermoelectric • Pyroelectric • Thermal Conductivity

However, on basis of absorption and interaction of materials with target gas molecules, we can classify the gas sensors into two other sub categories.

They are- I) Physical Sensor II) Chemical Sensor

.In Physical sensor no chemical reaction takes place at the receptor, and the signal is a result of a physical process, such as mass, absorbance, refractive index or conductivity change. Chemical sensors are based on chemical reaction between target molecule and receptor.

Interaction of target gas with the sensing material is one of the key factors determining the sensing behaviour of a material. Apart from external parameter like temperature, in general there are other several parameters related to material and substrate used to grow the film that

affect the gas sensing. Among them grain size, porosity, film thickness, surface geometry, film texture, active surface area are the major parameters to determine the sensitivity /response of gas sensing material [13].

4. Existing Ammonia gas sensors and their detection methods:

Existing gas sensors used to trace the ammonia is mostly metal oxide based (MOS) and operated at elevated temperature. Although metal oxide are preferred for their limited sensing range, good response but suffers from many disadvantages like high temperature operation, high power consumption, poor precision etc. Therefore, lots of effort is going on investigate to develop sensors to trace ammonia (NH_3) which are high sensitive, room temperature operable, high response with excellent selectivity tuning growth process, surface modification, engineering with other materials and dimensionality [14]. As nanostructure enhances the adsorption of the target gas due to higher surface area than their bulk counterpart, 1D nanostructure are also being incorporated to improve the performances of existing ammonia gas sensors. Reports are available on functionalization by carbon nanotube (CNT) (both single wall and multi wall CNT) on metal oxide semiconductor to enhance the response. Common metal oxide NH_3 gas sensors are WO_3, SnO_2, In_2O_3 but all works at temperature range typically between 50°C to 300°C[14]. Very few reports are available on room temperature gas sensor based on mainly PANI that too has poor sensitivity as compared to metal oxides. Along with this, all these sensors are based on electrical detection method which needs read out instruments. Not only ammonia sensors, most gas sensors are electrical based, few are optical. In following chart we are listing the different detection methods for detection that gas sensors follows (mostly metal oxide based).

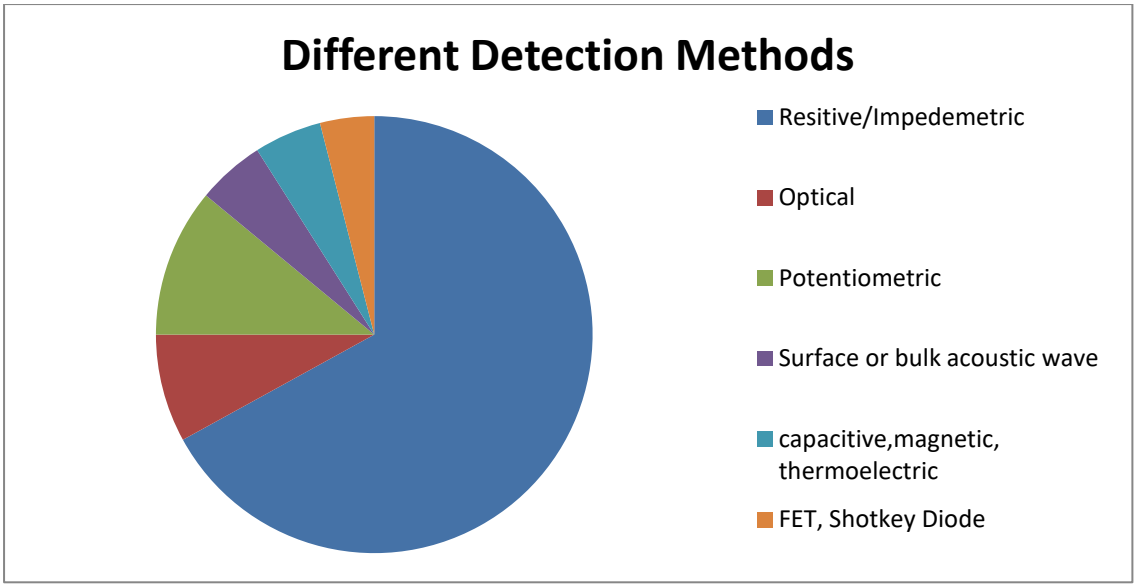

Figure 2: *Different Techniques for detection of ammonia gas*

Thus innovation and development of new gas sensor materials along with novel, easy detection method to trace ammonia working simultaneously room temperature operable and cost effective manner would be extremely rewarding. In following section we are going to describe a novel, cheap detection technique to trace ammonia by family of lead based perovskite halides which can be addressed as new material for solid state ammonia gas detector.

5. Brief review of Halide Perovskite :

Perovskite halides are probably the most sensational and well researched class of emerging materials since last decade for its unprecedented application potentials. High absorption coefficient, band gap tunability, long diffusion length make them outstanding candidate for photovoltaic and optoelectronic applications [15-16]. Also presence of both organic and inorganic components makes them exciting for both fundamental and application oriented research. Among them lead based hybrid halide perovskites are mostly attracted because of their stable tolerance factor relative to other B site cation (Sn, Mn).

The family of hybrid organic—inorganic perovskite materials introduces a molecular assembly of a well-defined nanoscale structure serving as an exemplary species to closely bridge these organic and inorganic worlds.

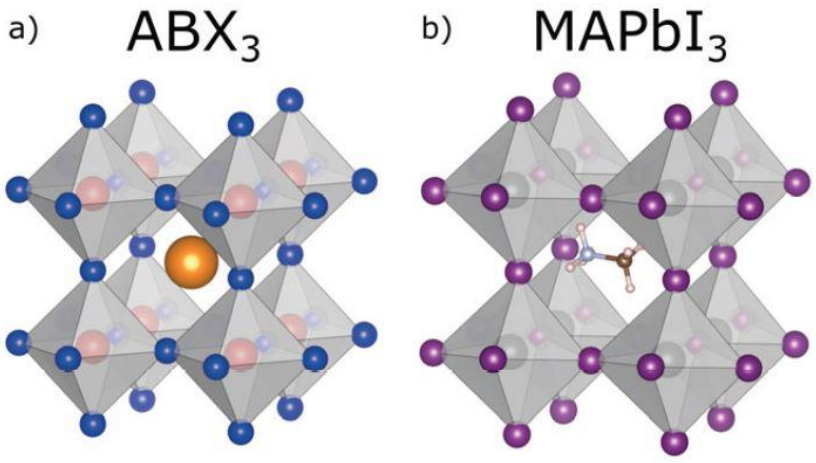

Figure 3. *Schematic of general crystal structure of halide perovskite; shown for $MAPbI_3$/MAPI [15]*

Perovskites are a large family of compounds that share the same chemical formula ABX_3. 'A' and 'B' denote cations, where A is much larger than B, and 'X' an anion. The versatility of perovskites makes them highly attractive as they can form multidimensional structures pertaining to the same chemical formula through use of different combinations of various components. A wide variety of elements may be incorporated each with different valency, so long as charge neutrality is satisfied, making perovskites one of the most highly studied materials [17].

Halide perovskites, as the name implies, employ an inorganic halide (I^-, Cl^-, Br^-) to replace the oxygen anion of oxide perovskites. An organic or inorganic monovalent A^+ cation and a divalent B^{2+} metal cation are generally seen corresponding to the 1^- charge of the halide anion [18].

There is a stringent structure-property relationship for perovskites pertaining to both crystal composition and ion arrangement that govern its structural, optical and electronic properties.

6. Perovskite Halide as gas sensor :

Research on these systems is mostly done in the area of solar cell and optoelectronic applications like photo detector, light emitting diode (LED) etc [15]. There are still some interesting areas of application which are not explored much. In this book chapter, we have

explored a new application potential of lead based perovskite halides in the area of gas sensor; as solid state detector with a new detection technique.

Here, we describe such paper based color change visual sensors can be made from family of lead based perovskite halide for easy and rapid detection of ammonia gas at room temperature. But the qualitative nature of sensing towards NH_3 remains the same for family of perovskites halides irrespective of substitution of cation and anion i.e nature of sensing is independent of crystal and electronic structure. The sensor is cheap and disposable. Since the sensor needs no electrical read–out and no external peripherals, it is field useable without need for trained operators. The innovation involves effective utilization of new class of materials like lead based perovskite halides which have not been utilized before for effective gas sensing.

We have already described the necessity of detection of hazardous environmental pollutants like ammonia (NH_3). Detection of the presence of NH_3 at a low level is most desirable as the presence of the gas can occur in several areas like refrigeration, food processing and storage, environmental protection, chemical technology, etc. Up to now most NH_3 sensing materials are metal-oxide semiconductor systems that are based on electrical sensing or optical detection and often suffer from low selectivity, room temperature operation and slow response/recovery rate and poor detection limit [19-21]. In that context investigation of new materials like perovskite halides for NH_3 detection at room temperature using paper with new detection technique based on visual color is an important innovative step forward.

In this chapter, we have studied/discussed in detail paper based visual gas sensing property and sensor characteristics by family of lead based perovskite halides using three different materials namely $MAPbBr_3$ (MAPB), $MAPbI_3$ (MAPI) and $FAPbI_3$ (FAPI) where effect of both anion and cation substitution on sensing performances has been reflected. All the three lead based perovskites change their pristine color in presence of NH_3 gas to a qualitative extent. The reason behind color change has also been investigated through series of experiments using spectroscopic and structural characterization tools to understand the sensing mechanism of these novel materials as gas sensor.

7. Growth of halide perovskite based paper sensors for efficient detection of ammonia:

We have studied the visual gas sensing property by the group of lead perovskite halides namely methyl ammonium lead iodide ($CH_3NH_3PbI_3$/MAPI), methyl ammonium lead bromide ($CH_3NH_3PbBr_3$/MAPB) and formamidium lead iodide ($CH(NH_2)_2PbI_3$/FAPI).

We adopted one step solution growth process to grow our paper based films using halide perovskites.

For one step solution growth process, first by equimolar lead Iodide (PbI_2) with methyl ammonium Iodide (CH_3NH_3I) are mixed at 1:1 molar ratio in dimethylformamide (DMF). Then paper substrate is spin or dip coated for ~30 sec to in the solution. Then, the coated substrates are kept at 100° C in an oven for ~ 20 minutes drying. Finally this forms the desired morphology on different substrates.

For MAPB , microstructured film has been synthesized by equimolar mixing of lead bromide ($PbBr_2$) with methyl ammonium bromide (CH_3NH_3Br) at 1:1 molar ratio in dimethylformamide (DMF). Then different substrates spin and dip coated for ~1 min to dip coat in the solution. Then, these spin/dip coated substrates are kept at 120° C in an oven for ~ 20 minutes drying. This helps to form the of MAPB micro structures on the paper substrate. Similar fashion was followed to synthesis of FAPI. The lead iodide (PbI_2) and formamidium iodide ($CH(NH_2)_2I$)/FAI were mixed in DMF. Rest process is same as MAPI film formation except annealing was done at 140°C.

We have shown the XRD and surface morphology of all three perovskites. Then these solution processed paper grown materials are cut into several pieces with similar size (typically $1\ cm \times 1\ cm$) to form the devices which are used to test the ammonia sensing property.

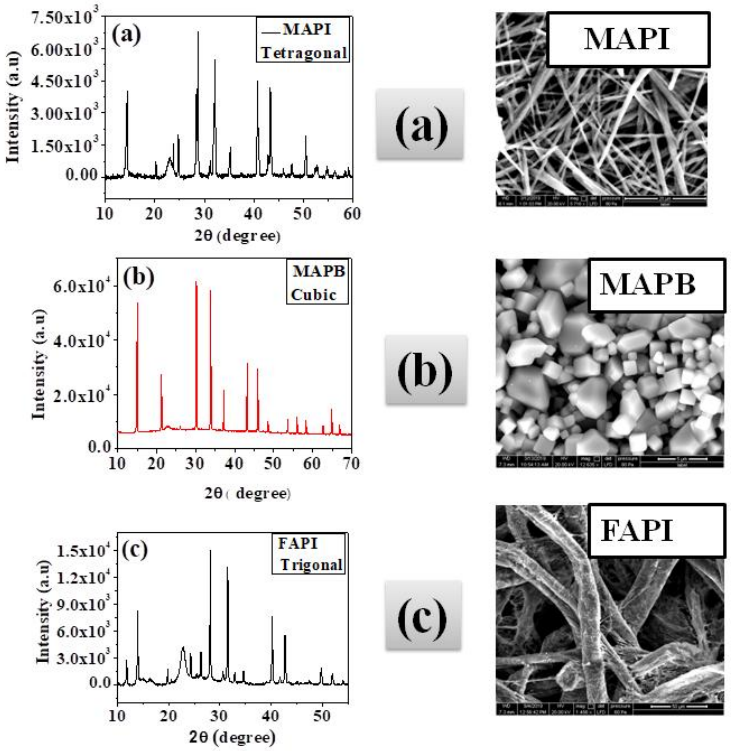

Figure 4. *XRD & FESEM images of pristine a) MAPI b) MAPB c) FAPI films grown on cellulose paper [9]*

8. Ammonia gas induced visual color change by family of lead based perovskite halides:

We show here, a quick, easy method of ammonia detection by simple visual color change method by paper based solution grown lead based perovskite halides. The main experiment in case of visual sensing is to measure the response time to change the pristine color.

The experiment was carried out in a homemade test chamber with controlled gas environment. Initially the test chamber was purged by injecting nitrogen (N_2) gas for a sufficiently longer time. Then calibrated amount of NH_3 (with a given concentration) was injected into the chamber. The calibration was done by using volumetric method.

All paper grown lead based perovskites (hybrid halide) change their color in presence of ammonia gas. Since, sensors are fabricated on paper, hence very cost effective. We have also shown qualitative nature of visual sensing remains same under alteration / substitution of cation and anion keeping B site cation (Pb) as fixed.

The color of the paper sensors made from all the three materials change on exposure to NH_3 gas and can be detected visually as shown in figure. MAPI & FAPI changes to yellow from their original black color whereas the pristine orange color of MAPB changes to white in presence of NH_3 gas. Hence all three materials under lead halide perovskites show the color change effect at room temperature.

To get insight more about visual response, we had carried out the experiment of all three micro/ nano structured films (MAPI, MAPB and FAPI) in identical environment at room temperature. All the three films were cut into identical size, shape and had been grown in same environment and exposed to equal concentration of NH_3 and recording the experiment in a video camera. From video we got the necessary response time to change the color of all three sensors. All compounds, irrespective of cation/anion substitution are able to detect NH_3 gas visually though the response time is different... It has been observed that for a fixed concentration (~80 ppm), among all three, MAPI shows very instantaneous response (< 1 sec), where MAPB has response time ~ 2 min and FAPI has higher response time (> 4 min) for complete change of the color from their pristine one as recorded from the video camera i.e. response time (τ) for MAPI $_{visual}$ < MAPB $_{visual}$ < FAPI $_{visual}$ [8].

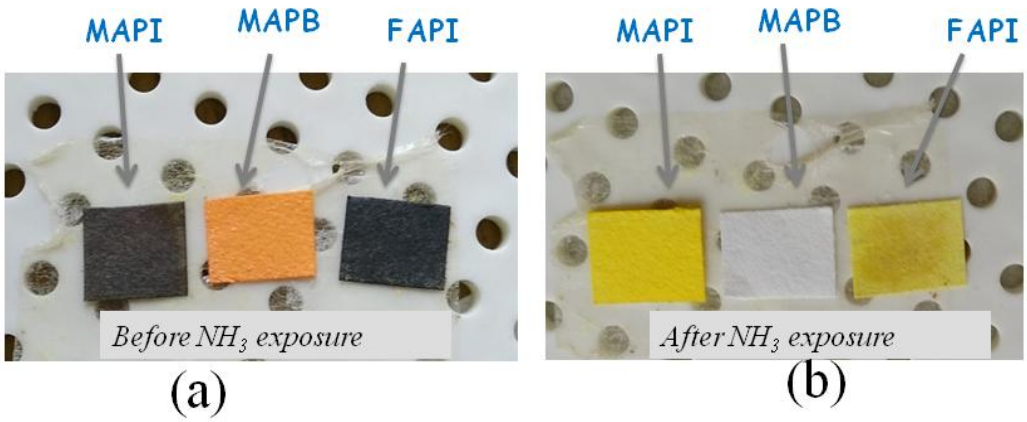

Figure 5. *Photographs of MAPI MAPB, FAPI films (a) before NH_3 gas exposure (pristine films) (b) after NH_3 gas exposure[9]*

It is also noteworthy that this color change phenomenon occurs in presence of NH_3 gas both in open atmosphere and as well as closed test chamber with suitable injection of NH_3.

The main results on visual sensing for all three lead based perovskites have been summarized as follows.

Parameters	MAPI	MAPB	FAPI
Crystal Structure	Tetragonal	Cubic	Trigonal
Surface Morphology	Nano/ Microrod	Microcube	Fibrous
Band Gap (in eV)	1.53	2.3	1.6
Base Specific Resistance (in $G\Omega/cm^2$)	139	0.8	0.4
Sensing Parameters			
Pristine Color	Black	Orange	Black
Color in NH_3 gas	Yellow	White	Yellow
Response Time (visual)	~10 sec	~2-3 min	$\geq$ 4 min
Corresponding Lead Halide in presence of NH_3	Lead Iodide (PbI_2)	Lead Bromide ($PbBr_2$)	Lead Iodide (PbI_2)

Table 1: Visual sensing parameters for lead based perovskite halides, MAPI, MAPB and FAPI paper sensors at ambient temperature

8.1 Color Change is a Surface Phenomenon:

In previous section 3 we have seen that surface morphology, film texture and dimensionality has severe /dominant influence on sensing performances on semiconductor gas sensor. Here we have examined these issues on visual sensing performances on lead perovskite paper sensors.

It has been noticed that, color change effect only occurs in the micro and nano structured thin films of the materials, which has larger surface area compared to their bulk counterpart. It also has been observed that for bulk the color change has no response. We have shown this effect with single crystalline MAPB sample. We observed that the single crystal did not show any color change in NH_3 atmosphere for normal/typical exposure time (~2-3 minutes). However for a sufficiently long exposure (~ 1 hr) time, upper face of the crystal gets slightly corroded but no colour change had been observed. Similar effect happened in case of other two bulk single crystals also. This provides an important inference that color change and hence visual gas sensing is predominant by the surface morphology. Respective photographs are shown in figure 6.

Figure 6: *Photographs of a) pristine single crystal MAPB b) NH_3 gas exposed MAPB for 2-3minutes and c) after exposure for sufficiently long time (~ 1 hr) without any color change[9]*

9. Detailed Study of Visual Sensor Characteristics Using Perovskite Halides:

From previous results we have seen MAPI has the best i.e the fastest response among all the lead halide perovskites. The reason for quantitative difference in response time will be discussed in later section. We extended our study to explicitly characterize the detail gas sensor characteristics using MAPI for its better response. In following section we have discussed the sensing characteristics of MAPI based paper sensor [10].

- **Investigation of concentration dependent Response Time** :

It is important to study the response (here response time) of a gas sensor as a function of concentration of target gas. It carries the information about dependency of sensor performance on concentration. We investigated the response time for color change at different NH_3 gas concentration by injecting NH_3 gas in the test chamber and response was similarly recorded through video camera as discussed earlier. Figure 7 shows the dependence

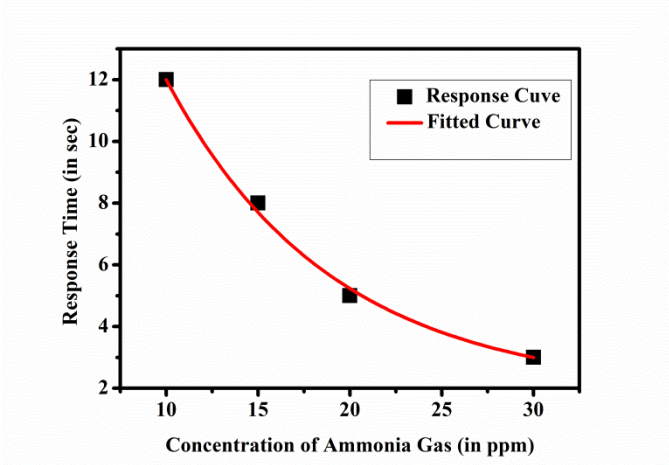

Figure 7. *Dependence of the time response of the paper sensor to different concentrations of NH_3 gas at room temperature[11]*

response time (respective time to change the color) τ of the MAPI paper sensor for different gas concentrations. It can be seen that for concentration of only 10 ppm the visual sensor changes its color within a response time of around 12 sec. Bare paper had no response of color change when exposed to NH_3 gas. Also below 10 ppm concentration of NH_3 gas, the color change effect did not occur. It has also been clearly observed as shown in figure that the MAPI sensor exhibits a faster response when exposed to higher concentrations of NH_3 gas. The response time τ shows an exponential dependence on concentration c such that,$\sim \exp(-c/c_0)$ (c_0 being a constant) so that with increase of the NH_3 concentration the response time quickly decreases.

- **Selectivity of the paper sensor to Ammonia Gas**

Selectivity is one of the major characteristic properties of a gas sensor. Selectivity of the visual sensor was tested by injecting different other hazards gases like Methane (CH_4), Nitrous Oxide (N_2O), Carbon dioxide (CO_2) etc in the test chamber each up to a concentration of 500 ppm for long time (~ 15 minutes or more). No visual color change had been observed in all these cases. This strongly suggests the visual gas sensor is highly selective to the NH_3 gas only. MAPI decomposes in presence of NH_3 and this does not happen with other gases. This ensures that the paper sensor has high level of selectivity towards NH_3.

- **Effect of Humidity**

Since perovskites are known for their degradation it is crucial to check the perovskite sensor response on humidity. Stability under exposure to moisture is an important parameter for its usability in an open atmospheric condition where there may be a likelihood of the moisture affecting the sensor. This effect of humidity on MAPI sensor was investigated in a controlled way by subjecting the sensor paper in the test chamber with different percentage of relative humidity (% RH). It was observed that no color change happened during exposure to humidity for RH range from 10% to 90%. In figure 8 we have shown photographs of the sensor paper when exposed to three different relative humidity (13%, 43% and 76%) as shown by the RH meter. The pristine black color of the sensor is maintained irrespective of the relative humidity (exposure time ~180 sec). In humid condition the sensor can response to visual color change when the sensor paper is exposed to NH_3 gas.

Figure8: *Photograph of paper sensor in atmosphere of varying humidity as shown by the RH meter reading.[11]*

a) At relative humidity 76% b) At relative humidity 43% c) At relative humidity 13%

- **Stability towards storage and shelf-life**

A number of sensor papers were stored in a vacuum desiccator. Temperature range tested between 20ºc to 35ºc for storage as well as for experiment. For testing the visual performances, one strip was taken out at interval of 15 days and then exposed to only 15ppm of NH_3 gas in the test chamber and response time was measured. We continued it for 180 days. The data are shown in figure 9. It can be seen that the response time of the paper sensor

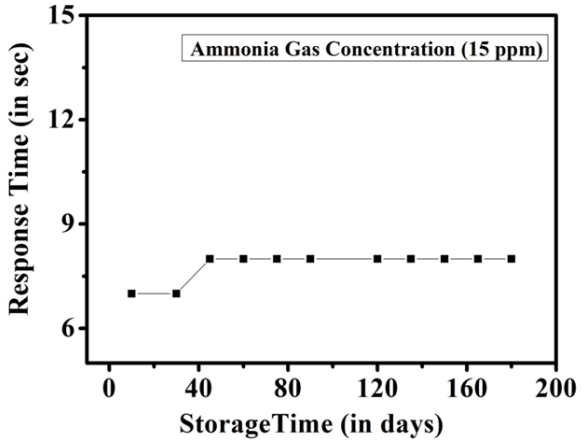

Figure 9: *Stability of the sensor against long term storage. Sensing study was performed at room temperature upon exposure to NH_3 gas of fixed concentration 15 ppm.[11]*

leading to visual color change(from black to yellow) is nearly constant after an initial small change (that occurs within about first 40 days). This small change in the response time however, does not affect its utility. The relatively high shelf -life and almost constant detection performance of the sensor can be concluded as usability of MAPI as standalone stable sensor for NH_3 gas at room temperature.

10. Discussions:

10.1 Investigation of Color Change:

The primary results on color change of MAPI, MAPB and FAPI on exposure to NH_3 indicate that there could be a phenomenon of conversion of corresponding lead based halides of the respective pristine perovskites since the converted color are similar to lead bromide ($PbBr_2$) and lead iodide (PbI_2). To rule out hypothesis and to get better insight we performed optical spectroscopic measurements.

- **Evidence from UV – Visible spectroscopy:**

The UV-Visible on pristine (unexposed) perovskite halides films of MAPI, MAPB and FAPI, exposed NH_3 films and corresponding lead halide films i.e. $PbBr_2$ and PbI_2 was done and has shown in figure 10 and figure 11 respectively. For all three cases the exposed film exhibits a very different optical absorption than that of unexposed films. For all cases data were taken in absorbance mode with solid sample attachment.

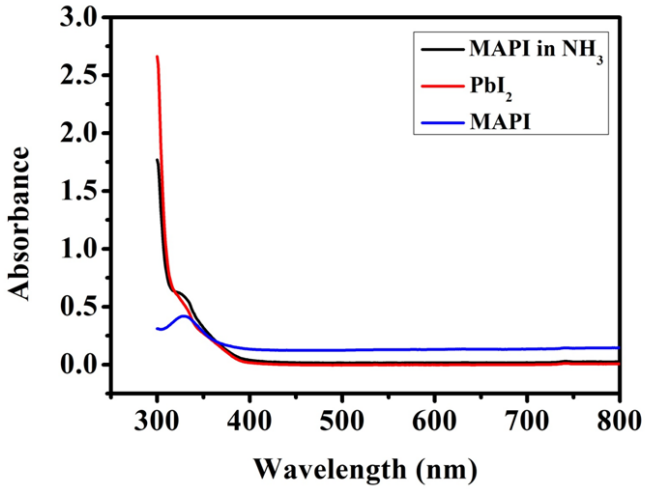

Figure 10: *Comparison of UV-VIS absorption of unexposed pristine MAPI on paper, NH_3 exposed MAPI and PbI_2 film on paper[11]*

MAPI film starts to absorb around 750-800 nm and strongly absorbs for wavelength below 500 nm. But in contrast the film exposed to NH_3, the absorbance of the film is nearly zero in the visible region and it starts to absorb only in the UV region for wavelength below 400nm. Comparison with the absorption spectra of the PbI_2 film shows that the NH_3 treated MAPI film has similar absorption spectra as that of the PbI_2 film. For the MAPB the pristine (unexposed) film starts to absorb around 575 nm whereas, the exposed film starts to absorb around 385 nm which shows very similar absorption spectra of $PbBr_2$ film. In case of FAPI also, where pristine FAPI (unexposed to NH_3 gas) shows substantially different absorption spectra than NH_3 treated FAPI film whereas, PbI_2 has identical absorption edge that is very similar to exposed FAPI film.

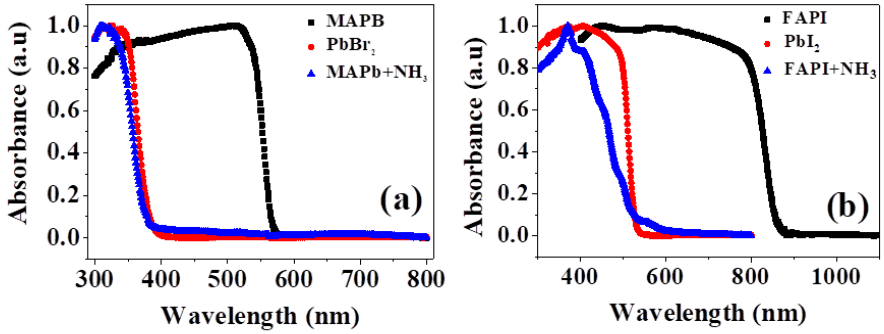

Figure 11. *a) Comparative study of UV spectra among pristine (before exposure), exposed MAPB and lead bromide ($PbBr_2$) film b) pristine (before exposure), exposed FAPI and lead iodide (PbI_2) films respectively[9]*

For three cases identical nature of absorption spectra of exposed films and the corresponding lead halide films suggests a firm evidence of our hypothesis.

- **Evidence from PL spectroscopy:**

To check further we performed PL spectroscopy for all three pristine perovskite lead halide films exposed films and corresponding lead halide films. Like absorption spectra, in case of PL we recorded the spectra of pristine, NH_3 treated and corresponding lead halide films.

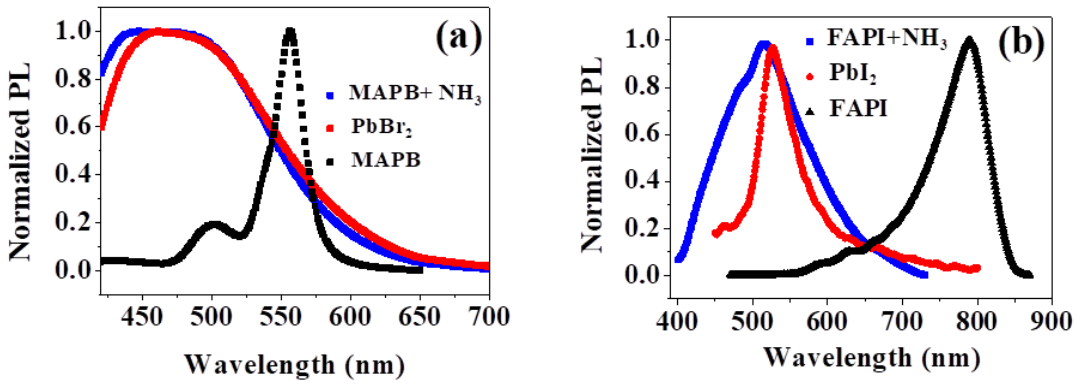

Figure12. *a) Comparative study of PL (photoluminescence) spectra of pristine, exposed MAPB and lead bromide ($PbBr_2$) film b) pristine, exposed FAPI and lead iodide (PbI_2) films respectively[9]*

PL spectroscopy shows the pristine (unexposed) MAPB film has PL peak around 557 nm and for exposed film, the PL spectra displays a broad peak around 470nm and which is identical with the spectra obtained from $PbBr_2$ film (figure 12.(a)). In case of FAPI (figure 12.(b)), the original (unexposed) film has a PL peak around 790 nm which is very different from the exposed FAPI film. Exposed FAPI film shows PL peak around 514 nm which is very much consistent with the PL spectra of PbI_2 film. Similarly, a comparison of the PL spectra of the NH_3 treated film (PL peak around 528 nm) with that of the PbI_2 films (532 nm PL peak) shows striking similarity of the two and again establishing that the dominant phase of the MAPI film on exposure to NH_3 gas is indeed due distinct color of PbI_2 phase. All three distinct PL spectra of three different materials along with exposed condition and respective halides has been shown figure 13.

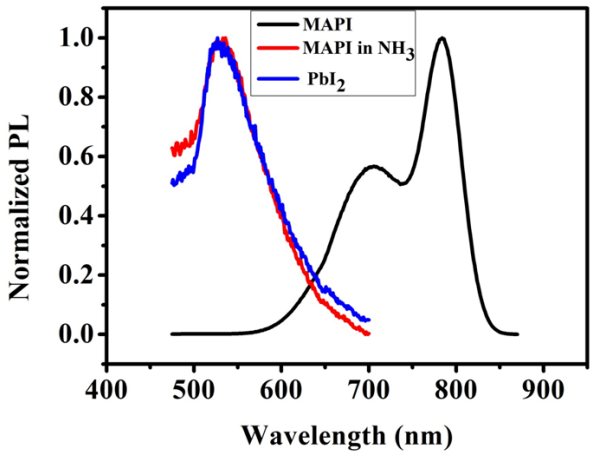

Figure 13: *Comparison of PL spectra of unexposed pristine MAPI on paper, exposed MAPI (to NH_3) and PbI_2 film on paper[11]*

The above two measurements establish a very firm evidence of decomposition / conversion of perovskites to their corresponding lead halides [8, 10].

- **Evidence from electrical readout:**

To corroborate our hypothesis on color change, the electrical I-V measurement on the exposed lead halide perovskites and corresponding lead halides have been performed. We tested the exposed MAPB film and corresponding lead bromide ($PbBr_2$) along with FAPI and lead Iodide (PbI_2) film. It has been observed that an I-V characteristic of exposed MAPB is analogous to $PbBr_2$ I-V characteristics; similar nature has also been observed for FAPI with PbI_2.For both cases current in exposed condition is significantly higher than unexposed condition although nature of contact remains ohmic. The data is shown in figure 14. These electrical measurements are further proof of conversion to corresponding lead halides during color change of lead based perovskites [8,10].

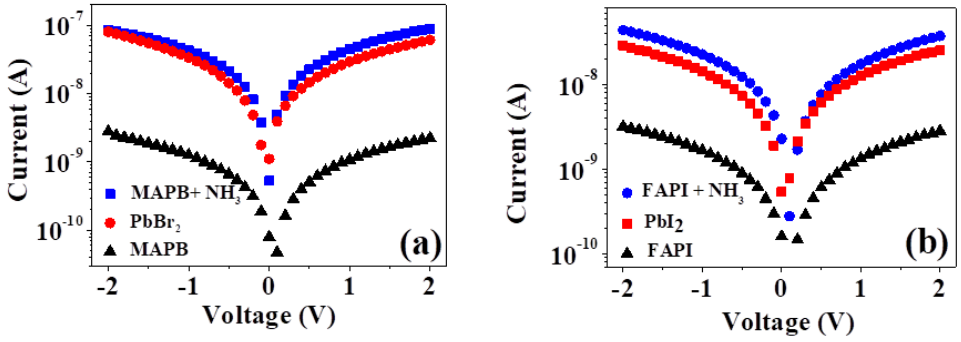

Figure 14. *Comparative study of I-V characteristics between a) pristine $PbBr_2$, exposed and unexposed MAPB film b) pristine PbI_2, unexposed and exposed FAPI film [9]*

11. <u>Novelty and utility of such gas sensor for detection of ammonia:</u>

The effective important aspects of this chapter are threefold. Firstly, use of family perovskite halide as active material for explicitly solid state gas sensor to detect ammonia is the major investigation. On other hand cellulose paper has been used in electronics since last century. Most common applications of cellulose-based materials are as dielectric for capacitors and super capacitors, permeable membranes in liquid electrolyte batteries or just the physical support of energy storage devices, organic thin film transistor (TFT) arrays inkjet-printed

sensors. But paper based gas sensor is an important invention. Thirdly, the method of detection of tracing gas sensor is quite unique. It just based on a simple color change, which is relatively simple without requiring any power gadgets and easy detection technique to trace a toxic pollutant.

As a visual sensor to assess the immediate extent of danger of presence of the NH_3 in an ambience, this is a desirable feature. Since three different materials has different detection limit, the sensors can be operated in three distinct region of ammonia concentration. If the concentration is very low one can use MAPI since it has lowest detection limit. The sensor takes nearly 10 secs (~ 10 ppm NH_3) to respond and this will not lead to detrimental exposure. On the other hand when the concentration is relatively high (~20-25ppm) and it approaches a danger level, the senor quickly turns color within 5 sec and gives a visual warning. For any operator in a hazardous environment this will give an immediate danger signal. For higher concentrations (more than 50 ppm) we can use other two sensors (MAPB and FAPI) instead of typical MOS and PANI sensors which show comparable detection limit but based on electrical read out.

The ability of the cheap easy to make paper based perovskite halide sensors to trace of NH_3 at room temperature with different detection limit at high selectivity and high sensitivity without any added electronics or need of any extra gadget, will have big impact and is of great practical relevance in areas of application where quick sensing is needed that no undue exposure will occur to NH_3.

12. Conclusion:

In summary, we have explored a new application potential of lead based halide perovskites in the area of solid state gas senor apart from its benchmark applications in optoelctronics. We have shown high sensitivity visual ammonia gas sensors can be made from family of Perovskite Lead halides with different anion and cation. The sensors are paper based using solution growth route and operable at room temperature. Since the sensors are easy to fabricate and being a visual color change sensors do not require any other extra equipment for its operation. Thus they can be used as rapid and selective detection of ammonia in a cost effective manner. We also established that visual response towards NH_3 gas is qualitatively independent of substitution/alteration of cation or anion, surface morphology, crystal structure, and electronic band gap. It has been proposed that NH_3 gas induced decomposition of material to the lead halides give rise to the color change of the material following a general

mechanism during interaction with NH_3. Thus this work shows that the lead based perovskite halide family could provide a general platform for room temperature (unheated) solid state NH_3 sensor with new detection method which is compatible with paper based technology.

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