

A new inorganic-organic hybrid halide perovskite thin film based ammonia sensor

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ABSTRACT

A new perovskite material based on ethylene-diamine-dichloride and lead iodide as organic and inorganic precursors respectively was synthesized. Thin films of perovskite material were characterized using SEM, UV-Visible spectroscopy, XRD, and FT-IR. Sensing properties of inorganic organic perovskite thin films were studied and it was found to be selective for ammonia detection. Ammonia being one of the most hazardous and volatile chemical becomes necessary to detect. Color change of perovskite film from yellow to orange was observed in the presence of ammonia vapors. Electrical measurements showed decrease in resistance in the presence of ammonia vapors. Low concentration upto 50 ppm can be easily detected in approximately 40 s. The present method for detecting ammonia is unique, simple, selective, low cost and can be easily implemented for the field studies.

1. Introduction

Hybrid organic inorganic perovskites [1–4] have been extensively studied for various device applications, such as, photovoltaics, LEDs and sensors during the last decade. In 3-dimensional perovskite structures, atoms align themselves in cubical crystal structure with the general formula AMX_3 , where A, M and X represents organic, metal and halide ions occupying the corner, centre and face-centre positions respectively. The perfection of cube is dependent on various factors such as reaction conditions, raw materials and technique used for fabrication of thin film [5,6]. Recently, 2-dimensional perovskites with general formula A_2MX_4 or BMX_4 , where A and B are monodentate and bidentate organic ion, respectively have been investigated [7]. Layered perovskites are made up of alternate inorganic and organic layers. Inorganic layer made up of $[PbX_6]^{4-}$ octahedra is stacked between organic layers and vice versa [7]. These materials are greatly tunable in terms of structural and optical properties. The crystal structure of inorganic-organic hybrid perovskites can be altered easily by changing A, B, M and X in structure and thus properties of these materials can be changed accordingly [7]. During the last few years tunable behavior of perovskite materials have also become popular in the field of sensors due to their ability to sense polar gases. Moreover, due to their high selectivity, sensitivity and reversibility researchers have studied sensing properties of organo-metallic halide perovskites for number of analytes such as 2,4,6-trinitrophenol and other hazardous chemical compounds

[8].

Ammonia is considered as highly toxic chemical in liquid as well as in gaseous phase because exposure to high concentration of ammonia causes immediate burning in nose, eyes, throat and even respiratory failure. Lower concentration of ammonia also results in irritation in respiratory system. Further it expands 850 times when released in ambient atmosphere which makes it more dangerous than other gases [9]. Therefore, different ammonia sensing techniques have been developed based on metal oxide nanostructures, conducting polymer etc. [10,11]. Metal oxide based sensor works on the principle of co-adsorption of ammonia as a result of interaction between ammonia and oxygen. The major drawback of metal oxide based ammonia sensors is their poor selectivity and temperature dependent behavior. Conductive polymer based sensors as reported in literature [11] also suffer decrease in sensitivity over time when exposed to ammonia and have longer response time of over few minutes. Ammonia sensing based on spectrophotometric and optical gas detection techniques are also available [12]. These sensors are faster and can detect the lower concentrations of ammonia but main disadvantage of optical gas sensors includes expensive and cumbersome instrumentation which is not easy to transport [13].

The interactions of various molecules such as water, oxygen, ammonia etc. with perovskite films have been recently reviewed by Zhang et al. [14]. It has been found that perovskite materials are fascinating choice for ammonia sensing application due to their advantages like

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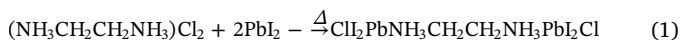
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appropriate electronic structure, processability, cost effectiveness, non-hazardous behavior and ability to sense ammonia at room temperature. Bao et al. [15] and Zhao et al. [16] reported perovskite based ammonia sensors. They studied optical and electrical changes induced by ammonia and suggested the associated mechanism based on phase transformation in the presence of ammonia. We report here a new perovskite for ammonia sensing application. The synthesis of a simple novel perovskite with bidentate ligand for the detection of ammonia vapors has been discussed. New perovskite based thin films were also tested for different concentrations of ammonia not reported previously. Color change of perovskite film from yellow to orange can be easily observed in the presence of ammonia vapors and the sensing response can be detected quantitatively by electrical conductivity measurements as well.

2. Materials and methods

Lead iodide (PbI₂) was purchased from Sigma Aldrich and ethylenediamine, hydrochloric acid (HCl), dimethyl sulfoxide (DMSO) and ammonia (NH₃) were procured from Thermo Fisher Scientific, United States. All the chemicals were used as purchased.

Organic precursor was synthesized by mixing 10 ml of HCl (11.65 M) with 60 ml of ethylenediamine with continuous stirring in an ice bath. White precipitates were obtained which were filtered. Precipitates were then dried in vacuum for 8 h at 60°C. Hybrid perovskite material was prepared by single step method by using organic (ethylene-diamine) halide and inorganic halide (PbI₂) as precursors. Both the precursors were dissolved in dimethyl sulfoxide in weight ratio of 1:2 and heated at 65 °C for 16 h with continuous stirring. To fabricate ethylenediamine lead iodide chloride (EDPIC) perovskite material, ethylene-diamine-dichloride and lead iodide were mixed in molar ratio of 1:2 in DMSO, according to the following reaction (1) and coated on glass substrate followed by annealing.



For ammonia sensing the thin films of perovskite material were deposited on pre-cleaned glass substrate from the solution prepared above by drop casting method and dried at 60 °C for 5 h. Contacts were made using copper wire glued with silver paste. Perovskite sample were characterized using SEM (FEI Quanta 200F), UV-Visible spectroscopy (Shimadzu RF-2600), FT-IR (Nicolet 6700) and XRD (Rigaku Ultima IV) studies.

3. Result and discussion

3.1. Fourier transform infrared spectroscopy (FT-IR) studies

Inset of Fig. 1 represents the molecular arrangement of synthesized perovskite material. As shown in figure, bidentate ethylene-diamine

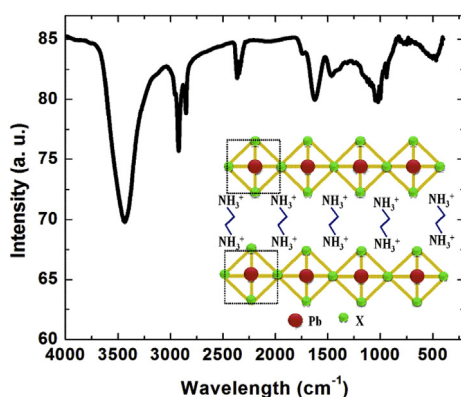


Fig. 1. FT-IR of EDPIC (Inset-Molecular representation of EDPIC).

cations act as bridge between two lead iodide octahedra by sharing the corners of adjacent perovskite unit cells [17]. The perovskite structure is stabilized by hydrogen-bonding between hydrogen atoms of diammonium organic cation and halide of MX₄ unit. This type of H-bonding is further confirmed by the FT-IR analysis. As shown in Fig. 1, the FT-IR spectrum of the perovskite thin film was recorded between 4000 and 500 cm⁻¹. The obtained spectrum is analogous to spectra reported in previous literature [18]. Peak at around 3439 cm⁻¹ corresponds to C-H stretching of alkyl chain. A band between 2850 and 2950 cm⁻¹ confirms the N-H—X (H-bonding) bonding between NH₃ of organic ion and halide of PbX₄ unit [19]. Peaks at 1630 cm⁻¹ and 1470 cm⁻¹ can be assigned to asymmetrical and symmetrical NH₂ deformation [20]. Band around 1035 cm⁻¹ and 941 cm⁻¹ arises due to C-N and C-C vibration, respectively. A weak band around 470 cm⁻¹ resulted due to gauche confirmation of ethylenediamine chains [21].

3.2. Scanning electron microscopy

Morphological changes were studied using scanning electron microscopy. Fig. 2 (a) and (b) show the SEM image of perovskite thin films before and after exposure, respectively. As shown in Fig. 2 (a) and (b) slight change can be seen in film surface after exposure of ammonia. The surface morphology of the film was found to be uniform after exposure as compared to unexposed film. This type of morphological change is also reported by Zhou et al. [22–24]. SEM micrograph also showed that synthesized material opted rod like structure shown in inset of Fig. 2. The solvent used for the perovskite synthesis was DMSO which is an aprotic polar solvent which supports the rod like arrangement of perovskite due to the solvophobic tendency of organic molecule and solvent which results in saturation of resulting material and thus faster precipitation. After saturation crystal grows only in one direction and thus leads to rod like structure [25].

3.3. X-ray diffraction

Crystal structure of thin film of perovskite material was examined using X-ray diffraction technique (Fig. 3) with CuKα radiation of wavelength of 1.54 Å. Peaks at 14° and 28.3° corresponds to (110) and (220) planes which shows the formation of layered perovskite [15,26]. The peaks obtained at 14°, 19.8°, 25.8°, 28.3°, 40.4° and 42.9° corresponds to (110), (112), (220), (224) and (314) in standard in-plane 2-theta scan are characteristic for a 3D perovskite [27]. Hence XRD gives the evidence of formation of regular tetragonal 3D-perovskite with lattice parameter $a = 8.929 \text{ \AA}$, $c = 12.685 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. Exposure to high concentration of ammonia resulted in degraded crystallinity of the film as shown in XRD after exposure.

3.4. Ammonia sensing studies of EDPIC

Ammonia sensing properties of perovskite thin film were studied using a setup given in Fig. 4 (a), which includes a mixing chamber to which ammonia gas and an inert gas were passed through inlet valves. Outlet of mixing chamber allowed the controlled flow of gas mixture to the detection chamber in which sample was placed and connected to electrometer interfaced with a computer. The sensing properties of perovskite sample were tested by placing samples in a detecting chamber to which ammonia gas was passed with argon as carrier gas. A Keithley electrometer (model-6514) interfaced with computer was used for resistance measurements of ammonia sensor. All the measurements were done at room temperature. Sensing measurements were done for different concentration from 50 ppm to 200 ppm of ammonia for different time intervals.

Color change from yellow to orange was observed when perovskite thin film was exposed to ammonia vapors. Fig. 4 (b) shows the change in color with increasing concentration of ammonia vapors. On exposing to lower concentration (50–200 ppm) of ammonia, color of perovskite

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