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Two-Dimensional Halide Perovskites for Heavy Metal Ions Sensing

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ABSTRACT
This report focuses on the exceptional trait of using perovskite halide sensing method in relation to sensing of heavy metal ions. Metal halide perovskite (MHP), which exhibits excellent sensing properties, is now considered as an efficient sensing material. We first describe the sensing of metal halides perovskites in metal halide. Next, performance improvement strategies focused on tuning of sensing properties for sensing metal ions. A new two-dimensional (2D) lead perovskite, $B_2A_{n-1}Pb_nX_{3n+1}$, exhibits impressive water resistance when in contact with water while retaining the real crystal arrangement and ocular characteristics. $B_2A_{n-1}Pb_nX_{3n+1}$. $B_2A_{n-1}Pb_nX_{3n+1}$ composites were synthesized and investigated for sensing. The results show an impressive increase in concentration in the composite and similar improvements in metal halide. Recent results in providing new watertight perovskite leads to secure, effective, and practical utilization of metal halide perovskite in sensing. In this project, we have synthesized compound $B_2A_{n-1}Pb_nX_{3n+1}$ (S1) and prepared perovskite films using a drop casting method. Then, we have performed sensing studies using heavy metal ions such as Cd^{2+}, Ba^{2+} & Zn^{2+} using UV-Visible (UV-Vis) spectroscopic techniques. From UV-Vis experiments, we have found that our synthesized receptor has sensed Cd^{2+} & Zn^{2+} but the receptor could not sense Ba^{2+}. We have also performed thin film colorimetric sensing experiment. We observed some amount of color changes for Cd^{2+} & Zn^{2+} ions. Thus, our synthesized receptor could be promising futuristic material for heavy metal ion sensing.

Keywords: Sensing, Two-dimensional, Metal halide perovskites, UV-Vis spectroscopy, Thin films

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INTRODUCTION

In the past decade, halide perovskite has fascinated remarkable attention as an all-around semiconductor. First naturally occurring perovskite in mineral form is $CaTiO_3$. The perovskite structure has mineral form having high potential in nature. In perovskite arrangement is essential for the addition of positive and negative ions should be equivalent to Zero of crystal network contend for metal halide perovskites (Bu 2022). Its exceptional physical and chemical properties have shown great prospective for sensing. With materials, we can tune the structure over a wide series which is important to improve the effectiveness of sensing (Satapathi 2018) and for photocatalysis (Zhu 2019, Irshad 2022). The low constancy and low sensing action of halide perovskites avoid this fault bearing substance from being used widely in sensing (Huang 2021). In some instances, sensing shows discoloration and decomposition due to presence of highly aromatic groups (Zhu 2018).

In our report, we reveal a highly stable sensing system based on two- dimensional (2D) halide perovskite $B_2A_{n-1}Pb_nX_{3n+1}$. Our halide perovskites with the general formula $B_2A_{n-1}Pb_nX_{3n+1}$ is 2D layered perovskite which demonstrates some amount of structural deviation (Maity 2021). "B" is the bulky ligand. "A" is site related to cations. "M" is metal cation and it is a divalent. "X" is a halide ion. Usually, layered perovskites are synthesized by changing the basicity of these compounds with a general formula (Fatema 2022). Stoichiometry of final material and the metal halide linkages are the basis of the structure of our product. These halide perovskite materials have a unique characteristic for their all-around dimensionality at both the inorganic and morphological framework (Yin 2017). This metal halide perovskites can be advantageous for gas sensors, and NO_2 detection (Shinde 2022, Cheng 2023).

In this work, we have synthesized perovskite receptor, $B_2A_{n-1}Pb_nX_{3n+1}$ (S1). The 2D perovskite films were prepared using a drop casting method, following heating. We have measured the absorbance of the S1 by UV-Vis double beam spectrophotometer in presence of different heavy metal ions analytes for sensing studies. We have also performed thin film sensing experiments to sense specific metal ion through observing the color changes in the film.

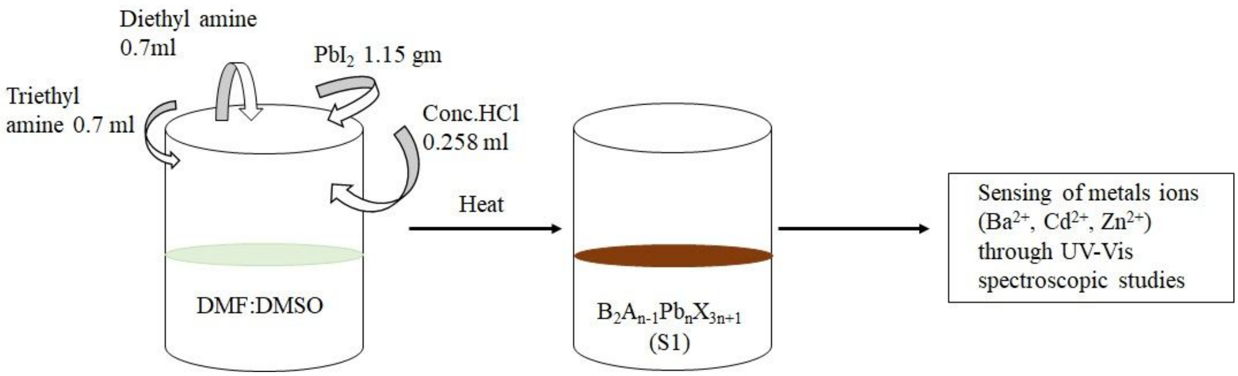
MATERIALS AND METHODS

Lead iodide, $ZnCl_2$, $BaCl_2$, $CdCl_2$, diethyl amine, triethylamine, DMSO, conc. HCl, ethanol, and acetone were all purchased from Avra chemicals. They were all used without further purifications. We have measured the absorbance of the synthesized materials by UV-Vis double beam spectrophotometer. We have performed the metal ion sensing such as Cd^{2+}, Ba^{2+} & Zn^{2+} studies using the same instrument.

Synthesis Procedure

Our perovskite $B_2A_{n-1}Pb_nX_{3n+1}$ (S1) was prepared by dissolving 0.387 ml of Dimethylamine, 0.516 ml HCl, 2.3 g PbI_2, and 0.347 ml, 0.0578g of Trimethylamine in the stoichiometric ratio of 5:3 of DMF and DMSO (scheme 1). For the synthesis of n = 4-layered films, pre-solutions (35wt%) were synthesized by dissolving PbI_2, Dimethylamine and Trimethylamine at a stoichiometric ratio of 4:3:2 in 5:3 ratio of DMF + DMSO (Yukta 2021). Conc. HCl is added to adjust the mole ratio. DMSO was used as a solvent for study in UV-Vis spectrometer. The 2D perovskite films were made-up using a drop casting process, following heating (Figure 2). The first substrate was pre-heated at 60 °C, and then, 100 μL of perovskite solution S1 was dropped onto the initial sample and started annealing at 50 °C for 15 minutes. Then, coated analytes were exposed to analytes.

RESULT AND DISCUSSION



Scheme 1: Synthesis process for compound S1

Our studied perovskite material has been synthesized by solution processed method using different amines such as diethyl and triethyl amines, $PbCl_2$, conc. HCl in DMF: DMSO medium by heating at 50 °C for 10 minutes. The initial light-yellow solution turned into dark blackish-red indicating formation of our investigated material (Figure 1). UV-vis spectrum supports the formation of our desired material.

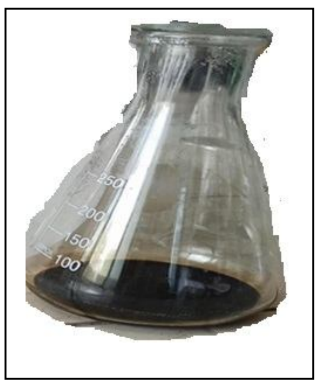


Figure 1: Synthesized S1 solution Sensing studies

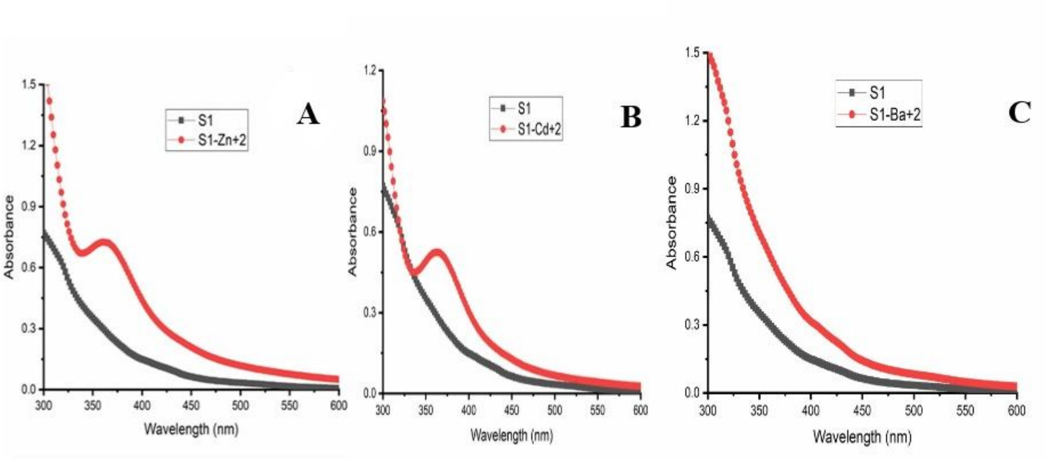


Figure 2: (A) Zn^{2+}, (B) Cd^{2+}, and (C) Ba^{2+} ions sensing studies

In UV-Vis spectroscopies studies, a new peak arises around 365 nm in comparison to S1 indicating formation of new ground state complex upon addition of Zn^{2+} ions (Figure 2A). Thus, our synthesized receptor senses Zn^{2+} ions.

In another case, a new peak arises around 360 nm in comparison to S1 indicating formation of new ground state complex upon addition of Cd^{2+} ions (Figure 2B). Thus, our synthesized receptor has shown response to Cd^{2+} ions.

But, no new peak arises in comparison to S1 indicating formation of no ground state complex upon addition of Ba^{2+} ions (Figure 2C). Thus, our synthesized receptor could not sense Ba^{2+} ions.

Thin films for on-site sensing

We have prepared thin film of S1 (Figure 3A) following the pre-mentioned method. We have studied sensing of analytes through measurement of digital images and changes in color of the S1 films after exposing to studied analytes (Figure 3B, 3C, and 3D).

We have observed color changes for our studied S1 films after exposing to Cd^{2+}, and Zn^{2+} (Figure 3B and 3D). We have not observed any such change for Ba^{2+} exposure (Figure 3C). Therefore, we can conclude that our thin films can sense Cd^{2+}, and Zn^{2+} in field applications through simply color changes.

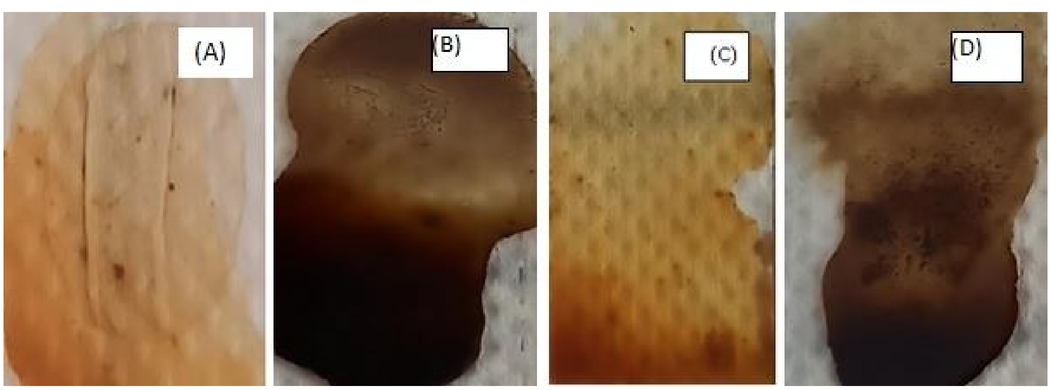


Figure 3: S1 coated films (A) after addition with (B) Cd^{2+}, (C) Ba^{2+} & (D) Zn^{2+} solution, followed by drying

CONCLUSION

In brief, we have synthesised 2D compound $B_2A_{n-1}Pb_nX_{3n+1}$. We have performed UV-Vis experiment with metal ions such as Cd^{2+}, Ba^{2+} & Zn^{2+}. From UV-Vis experiments, we have found that our material has sensed Cd^{2+} & Zn^{2+} selectively among the other analytes. We have also prepared thin films to sense metal ions through color changing for onsite sensing. In that case, we have observed significant amount of colour changes for Cd^{2+} & Zn^{2+} ions. Thus, our material has huge potential as a futuristic material for heavy metal ions sensing.

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