# Development of lead-free stable hybrid organic-bismuth halide perovskite for photo-voltaic application

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Organic-inorganic halide perovskite archetypically $CH_3NH_3PbX_3$ (X=Cl, Br or I) have shown remarkable performance in optoelectronic devices, particularly in solar cells where the solar to electrical power conversion efficiency reaching >20%. However, due to the toxicity issue associated with Pb, the real world application of these materials can be difficult. Therefore there is a need to create, investigate and optimise sustainable nontoxic perovskite materials for solar cell application. To this end, we have prepared Hexyldiammonium bismuth iodide ($HDABiI_5$), developed the protocol to make thin-films and investigated the application of Hexyldiammonium bismuth iodide ($HDABiI_5$) as an absorber in solar cell applications.

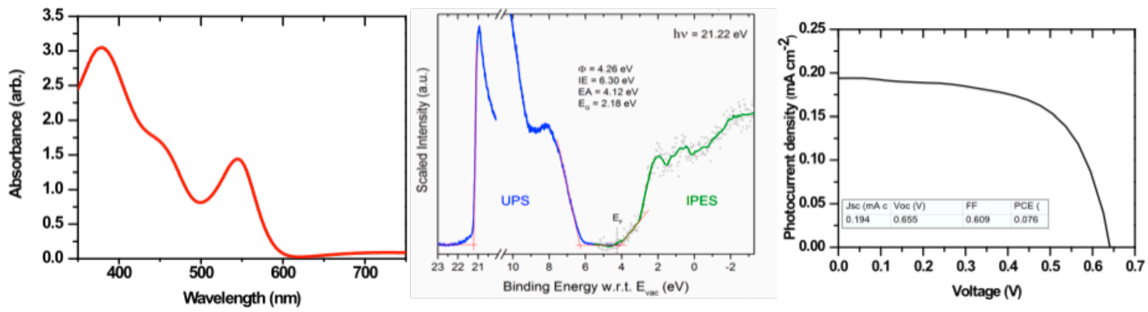
Materials development and characterization: Hexyldiammonium iodide salts were synthesised as follows. Hexyl diamine (0.05 moles) was dissolved in 100 ml ethanol, then HI (2.2 moles of acid per mole of diamine) was added drop wise into the ethanol solution. The resulting solution was stirred for 30 min. Then solution was allowed to dry at 90 °C in a beaker and the resulting salts were collected. Precursor solutions of the perovskites were formed by mixing $BiI_3$ and the Hexyldiammonium iodide salts in a molar ratio of 1:1.05 in anhydrous N'N-dimethylformamide (DMF). The solution was stirred until a clear red solution was formed. Single crystals of $HDABiI_5$ were prepared by slow evaporation of the precursor solution in DMF. The single crystal analysis of the compound shows that corner sharing $BiI_6$-octahedras form one-dimensional zig-zag chains and the hexyl diammonium cations fills the space between the inorganic chains.

Development of thin film: We prepared the thin film of the material by spin -coating the precursor solution on to a substrate followed by annealing on a hot plate. We found that the texture and crystallinity of the thin film can be tuned by adjusting the moisture content during the spin-coating condition. Immediate annealing of spin-coated films results in crystalline films where as a 2 min delay gives amorphous films. Thin film absorption spectrum (Fig. 1a ) shows intense absorption around 545 nm which can be attributed to strong excitonic nature of the material due its lack of 3D structure unlike the $MAPbX_3$ . We did not see any change in absorption spectra of the thin film of the Bi perovskite materials when stored in the ambient condition for several weeks unlike $MAPbI_3$ . UPS and IPES spectra of $HDABiI_5$ on FTO (shown in Fig. 1b) reveal that the Ionization potential (IP) and electron affinity (EA) of $HDABiI_5$ are 6.30 and 4.12 eV, respectively.

Solar cell performance: We prepared solar cell using $HDABiI_5$ as absorber, mesoporous $TiO_2$ as electron transporting and Spiro-OmeTAD as hole transporting materials. We show a representative current voltage curve of the solar cell in Fig. 1c. Though the material shows some photovoltaic behaviour, the performance is way below than that of the champion perovskite materials based on $MAPbI_3$ and $MAPbBr_3$.

The low solar cell efficiency could be attributed to strong excitonic nature of the $HDABiI_5$ where the generation of free charge carriers requires a heterojunction with energy offset is more than the exciton binding energy. Energetics at the $TiO_2$: $HDABiI_5$ interface may not be suitable for efficient charge separation. We also found presence of metallic Bi in the thin films which can act like recombination centres. Surface Photo-voltage spectroscopy shows presence of sub-band gap states in these materials. These sub bandgap state can also act like non-radiative recombination centres.

In conclusion, we have developed a nontoxic semiconducting Bi-based perovskite material which has potential application in solar cells. As this material is at a preliminary stage of development, further improvement in material quality and use of other type of electron acceptor materials can improve the efficiency of Bi-perovskite based solar cell .




a b c

Figure 1: (a) Absorption spectrum of $HDABiI_5$ thin film on glass (b) UPS and IPES spectrum of the thin film on FTO (c) Current density- voltage curve of a solar cell that uses $HDABiI_5$ as absorber, mesoporous-$TiO_2$ as electron transporting and Spiro-OmeTAD as hole transporting material