

**ABSTRACTS  
(POSTER  
PRESENTATIONS)**

# All-Solid-State Mechanochemical Synthesis and Post-Synthetic Transformation of Inorganic Perovskite-type Halides

**Provas Pal, Paribesh Acharyya**, Ananya Banik, Arka Sarkar, Sujoy Saha and Kanishka Biswas\*  
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All-inorganic and hybrid perovskite type halides are generally synthesized by solution based method with the help of long chain organic capping ligands, complex organometallic precursors and high boiling organic solvents. Here we demonstrate a room temperature, solvent free, general, and scalable all-solid-state mechanochemical syntheses and characterizations of different inorganic perovskite type halides with versatile structural connectivity in three (3D), two (2D) and zero (0D) dimensions. We have synthesized 3D CsPbBr<sub>3</sub>, 2D CsPb<sub>2</sub>Br<sub>5</sub>, 0D Cs<sub>4</sub>PbBr<sub>6</sub>, 3D CsPbCl<sub>3</sub>, 2D CsPb<sub>2</sub>Cl<sub>5</sub>, 0D Cs<sub>4</sub>PbCl<sub>6</sub>, 3D CsPbI<sub>3</sub> and 3D RbPbI<sub>3</sub> by this method. The all-solid-state synthesis is materialized via an inorganic retro synthetic approach, which directs to decide on the solid-state precursors (eg. CsX and PbX<sub>2</sub> (X = Cl/Br/I) with desired stoichiometric ratios. The mechanochemical synthesis of halide perovskites can be scaled up to ~1g of pure product in a single reaction. Moreover, we have performed post-synthetic structural transformations from 3D to 2D and 0D perovskite halides by the same mechanochemical synthesis at room temperature. The synthesis is carried out without the use of any solvent, capping agent and hazardous chemical. The present mechanochemical synthesis can be extended to other Pb-free halides and complex inorganic halides such as Ruddlesden-Popper perovskite phases.

**Reference:** Provas Pal, Sujoy Saha, Ananya Banik, Arka Sarkar, and Kanishka Biswas, *Chem Euro J*, 2017. Under revision.

# Solvent Engineering of Mixed Halide Perovskite Precursor Solution for Application in Solar Cells

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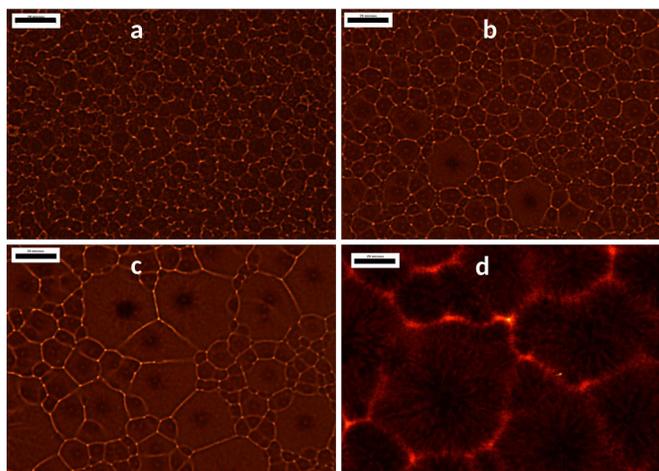
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## Abstract

Formation of large grain perovskite film with less grain boundaries, traps and smooth surface is a major challenge for obtaining excellent device performance in planar perovskite solar cell application. Researchers across the globe have employed various methods for the formation of large grain perovskite films. One such method is solvent engineering and treatment of film at various stages.<sup>1,2</sup> In this work, we have focused on mixed solvent engineering of the precursor solution using mixed halide perovskite. This precursor solution was later used for active layer coating by hot casting method. The results obtained through JV characterization suggests that varying ratios of DMSO in mixed halide perovskite solution with DMF plays a crucial role in improvement of device parameters. The results were further verified by microscopic images (Figure) where millimeter size domain of perovskite thin film were obtained with solution having DMSO, whereas the domain size without DMSO was found to be comparatively smaller.



Optical microscopic images of perovskite films with different DMSO concentration (Scalebar= 20  $\mu\text{m}$ )

## References

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### 3. Large area uniform MAPbI<sub>3</sub> thin films for Perovskite solar cells using two step technique.

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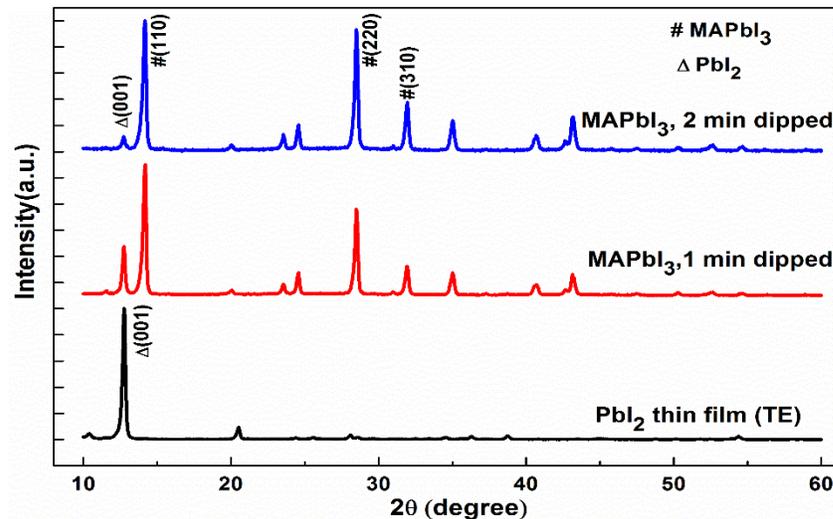
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9. Perovskite solar cell (PSC) is an emerging technology in photovoltaic, which uses perovskite structured hybrid compound as a light absorbing material (such as methylammonium lead halide). Perovskite solar cells with recorded certified efficiency of 22.1 % is the fastest advancing solar technology to date. The main advantage of such solar cells is that it has simple and cost effective fabrication method using solution process technique, such as spin coating. But the PSCs made by solution process have limitation of small device area due to porosity and non-uniformity in absorber layer. Pinhole-free layers can significantly improve the performance and stability of MAPbI<sub>3</sub> based perovskite solar cells. Thus to improve the quality of the absorber layer of PSCs, we have used two step method. First is thermal evaporation (TE) of PbI<sub>2</sub> and dip coating (DC) in methylammonium iodide (MAI) to convert it into methylammonium lead iodide (MAPbI<sub>3</sub>). The complete formation of MAPbI<sub>3</sub> after dipping PbI<sub>2</sub> film into MAI solution can be seen from XRD patterns shown in figure 1 below. Optical, structural and electrical properties of the MAPbI<sub>3</sub> films are also studied. This method of making perovskite layer can help in better performance of a PSC, as the films has uniform coverage.

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11. Keywords: MAPbI<sub>3</sub> Perovskite, thin film, thermal evaporation.

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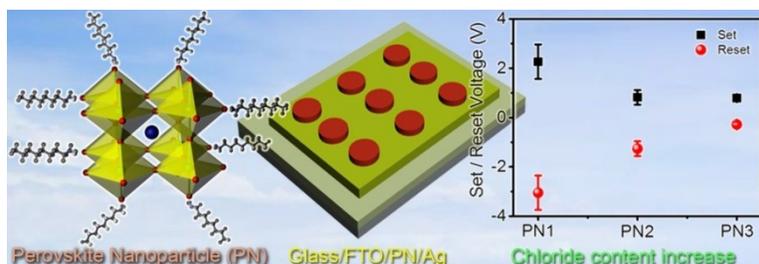
14. Figure 1: XRD patterns of PbI<sub>2</sub> and MAPbI<sub>3</sub> thin films with variation in dipping time.

# High-Performance Resistive Random Access Memory Devices from Hybrid Perovskite Nanoparticles: Control of Operational Parameters through Chloride Doping

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**ABSTRACT:** Organic-inorganic hybrid perovskites are the new wonder materials finding applications in advanced devices such as solar cells, light emitting diodes, photodetectors and field-effect transistors.<sup>1</sup> In the present work, we describe the use of hybrid lead halide perovskite in nanoparticle form for high-performance, air-stable, non-volatile memory devices through low-cost solution processing technique at ambient conditions. The resistive random-access memory devices fabricated from  $\text{CH}_3\text{NH}_3\text{PbBr}_{3.0}$  exhibited remarkable bipolar and bistable resistive switching behavior with small on-off voltage (2.66 V). Interestingly, the write-erase voltages of the devices were reduced to 1.04 V and further to 0.53 V by replacing bromide with chloride ions in the basic structure of the nanoparticles ( $\text{CH}_3\text{NH}_3\text{PbBr}_{2.54}\text{Cl}_{0.46}$  and  $\text{CH}_3\text{NH}_3\text{PbBr}_{1.97}\text{Cl}_{1.03}$ , respectively). Though the on-off voltage dropped, the on/off ratio, retention and endurance of the devices enhance on chloride doping. Our studies proved that hybrid perovskites are excellent candidates for developing low-cost non-volatile memory devices. It also illustrates the possibility to control the operational parameters of the devices through chemical modifications.<sup>2</sup>



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2. C. Muthu, S. Agarwal, A. Vijayan, P. Hazra, K. B. Jinesh, V. C. Nair, *Adv. Mater. Interfaces* **2016**, 3, 1600092.

## Structural tailoring of two-dimensional all-inorganic halide perovskites for photovoltaic devices

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In the present scenario, solar cells with organic-inorganic perovskite light harvesters have become prominent contenders for cost effective photovoltaic devices, by acquiring ~22.1% power conversion efficiency in a very short time domain. Though these devices have shown efficiency comparable to commercially available Si based solar cells on laboratory scale but ambient stability of these devices remains one of the major issues. Therefore a meteoric rise in the development of all-inorganic perovskite materials has been observed as a promising alternative due to their excellent optoelectronic and ambient stability. Herein colloidal synthesis of two-dimensional (2D) all-inorganic cesium lead halide ( $\text{CsPbX}_3$ ; X = Br, I) perovskite nanosheets of lateral dimension of few hundreds of nanometer and thickness of 8-15 nm were developed by altering the ligand ratio. The as-synthesized  $\text{CsPbX}_3$  nanosheets exhibit bright photoluminescence with broad wavelength tunability by composition modulation. To demonstrate their applications in photovoltaic devices, solar cells were fabricated using these nanosheets as photoactive materials. Our findings suggest that modulation of dimensionality of 2D nanosheets highly influence the device performance.

# Chemically Tailoring the Dopant Emission in Manganese-Doped CsPbCl<sub>3</sub> Perovskite Nanocrystals

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## ABSTRACT

Doping in perovskite nanocrystals adopts different mechanistic approach in comparison to widely established doping in chalcogenide quantum dots. The fast formation of perovskites makes the dopant insertions more competitive and challenging. Introducing alkylamine hydrochloride (RNH<sub>3</sub>Cl) as a promoting reagent, precise controlled doping of Mn(II) in CsPbCl<sub>3</sub> perovskite nanocrystals is reported. Simply, by changing the amount of RNH<sub>3</sub>Cl, the Mn incorporation and subsequent tuning in the excitonic as well as Mn d–d emission intensities are tailored. Investigations suggested that RNH<sub>3</sub>Cl acted as the chlorinating source, controlled the size, and also helps in increasing the number of particles. This provided more opportunity for Mn ions to take part in reaction and occupied the appropriate lattice positions. Carrying out several reactions with varying reaction parameters, the doping conditions are optimized and the role of the promoting reagent for both doped and undoped systems are compared.

# **Pre-programmed and Precise Size Control of Thermally Stable CsPbBr<sub>3</sub> Nanocrystals**

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## **ABSTRACT**

Adopting the concept of bonding of ammonium ions with halide rich surfaces of perovskite nanocrystals, preformed alkylammonium bromide is explored as a ligand, source of Br<sup>-</sup> ions and the precise dimension controlling reagent for the high temperature phase stable colloidal synthesis of all inorganic lead bromide perovskites. Interestingly, this turned out to be a robust controlling approach which led to wide window tunable nanostructures of CsPbBr<sub>3</sub> even with ~1 nm step growth regimes, just as a function of the concentration of added alkylammonium bromide salt. The controlling ability of size phase and the luminescence stability were observed superior in comparison to all previously reported temperature variable synthesis. While their size is tuned for cube shape, the width also varied in sheet structures. Being these are ionic solids and form instantaneously, the high temperature synthesis for the dimension tunable all inorganic lead halide perovskites are important and remained challenging. In this aspect, this method turned out to be more facile in comparison to all such reports which typically required change in reaction conditions or precursors/ligands variations.

# Effect of Plasmonic Metal Nanoparticles on the Performance of Inverted Perovskite Solar Cells

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## Abstract

Organic-inorganic halide perovskites have drawn tremendous research attention over the past few years for their extraordinary performance in solar cell, LED, photodetector and other emerging optoelectronic applications. Herein, we have studied the effect of plasmonic metal nanoparticles (NPs) in “inverted” planar perovskite solar cell performance. Silver (Ag) and gold (Au) NPs were synthesized by citrate reduction method from their corresponding salts. TEM and FESEM analysis shows uniform size distribution of Au (~10 nm) and Ag (~13nm) NPs. Au and Ag NPs show very strong plasmonic absorption peak at ~522 nm and ~432 nm, respectively, which are used for enhanced light harvesting in perovskite solar cell. Different amount of Au and Ag NPs solution were mixed with PEDOT:PSS hole transport layer and spin coated on patterned FTO coated glass. Compared to conventional FTO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PC<sub>61</sub>BM/Al device, Au and Ag doped PEDOT:PSS perovskite solar cell shows improved performance due to the enhance light harvesting by plasmonic NPs. Details of the characterizations results will be presented. Our work is expected to stimulate further investigation for plasmonic perovskite solar cells.

# Anomalous Optical Properties of Mn Doped MAPbCl<sub>3-x</sub>Br<sub>x</sub> Nanocrystals

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In hybrid perovskites, the nanocrystals (NCs) of MAPbCl<sub>3</sub> are less extensively investigated compared to that of MAPbI<sub>3</sub> and MAPbBr<sub>3</sub>, since this system is known to have a lower quantum efficiency compared to the other two. MAPbCl<sub>3</sub> is also less suitable for solar cell applications due to its large bandgap and the consequent limited absorption of the solar spectrum. In contrast, Mn-doped MAPbCl<sub>3</sub> has been investigated extensively for its interesting optical properties. We report here a slightly-modified room temperature synthesis of colloidal Mn-doped methylammonium lead halide (MAPbCl<sub>3-x</sub>Br<sub>x</sub>) perovskite NCs over a range of x-values. These were prepared by varying the Pb to Mn feed ratio and the reaction temperature. The Mn<sup>2+</sup> doped NCs show bright Mn<sup>2+</sup> emission with PL quantum yield of ~13%, suggesting an efficient energy transfer from exciton to Mn<sup>2+</sup>. Further, the temperature dependent PL results reveal an anomalous behavior in Mn<sup>2+</sup> PL emission, with a decreasing intensity with the lowering of the temperature. Time resolved measurements also contrast PL features with different origins, providing an understanding of the underlying mechanisms of PL properties of this class of NCs.

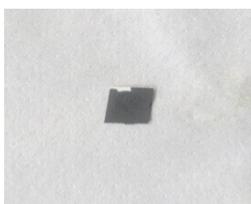
## Study of synthesis & gas sensing property of Methyl ammonium Lead Iodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) thin film

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Recently, a tremendous interest is growing on the development of hybrid lead halide perovskites as a promising class of materials for photovoltaic, optoelectronic application [1-2]. Herein, we have synthesized fully inorganic-organic perovskite halide methyl ammonium lead iodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) material via a room temperature solution approach. X-ray diffraction (XRD) is used to determine the tetragonal phase of the above material. Field emission scanning electron microscope (FESEM) was used to study the surface morphology of the nanostructured thin film. We have studied the gas sensing property of the material. A visual color change effect of the films on a porous substrate in ammonia gas environment with quick response time has been observed with high selectivity. [3]



Before put in ammonia environment



In presence of ammonia environment

### References:

[1] Andrew Barnabas Wong, Minliang Lai, Samuel Wilson Eaton, Yi Yu, Elbert Lin, Letian Dou, Anthony Fu, and Peidong Yang, *Nano Lett.* 2015, 5519-5524

[2] Qi Chen, Nicholas De Marco, Yang (Michael) Yang, Tze-Bin Song, Chun-Chao Chen, Hongxiang Zhao, Ziruo Hong, Huanping Zhou, Yang Yang; *Nano Today*, 2015, 10, 355-396

[3] Patent Applied "Ammonia Gas Sensor and A Method for Manufacturing the Same" Avishek Maity, Arup Kumar Raychaudhuri and Barnali Ghosh; Country-INDIA, File No-201731000270

## Overcoming recombination limited photocurrent generation in CsPbX<sub>3</sub> nanocrystal based arrays.

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Lead halide based perovskite nanocrystals (NCs) are promising photoabsorbers in designing high efficiency photovoltaic solar cells with large open circuit voltage (>1 V). However, very little work has been dedicated to the basic understanding of conductive properties of NCs in an ensemble system. Both DC and time resolved photocurrent measurements demonstrate that the photocurrent generation in these perovskite nanocrystal arrays is limited by the large excitonic binding energy of the material which thus limits the lifetime of the photogenerated electron hole pairs. As a result, nanotrench electrodes are employed as a strategy wherein device size is made to fit within the obtained diffusion length of the material in order to boost the exciton dissociation efficiency manifested by an enhancement of the photoresponse by a factor 1000. While both DC and time resolved photocurrent measurements pledge for defect tolerant nature of CsPbX<sub>3</sub> NCs, to further investigate the intrinsic nature of these colloidal semiconductor NCs, we then investigated the electronic spectrum in absolute energy scale using photoemission measurements in one of the representative CsPb(Br<sub>0.65</sub>I<sub>0.35</sub>)<sub>3</sub> NC arrays and revealed that indeed Fermi level lies in the mid-gap region but slightly shifted towards conduction band. The obtained work function ( $\approx 4.1$  eV - vacuum level vs. Fermi energy) can be further used to probe and quantify Schottky barriers at the metal-NC interface.

# **Solid state Mn<sup>2+</sup> ions doping in APbBr<sub>3</sub> perovskite nanocrystals: Triggering the efficient Mn<sup>2+</sup> emission through radiative pathway**

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Inorganic and organic-inorganic hybrid perovskites nanocrystals (NCs) have taken a quantum leap forward in the light-emitting diodes and display applications. The phenomenon of doping in these perovskite NCs could lead to the production of excellent materials for application in magneto-optoelectronic devices. Although there have been few successful attempts in solution based Mn<sup>2+</sup> ions doping in perovskite NCs, still no method is available for directly doping Mn<sup>2+</sup> in APbBr<sub>3</sub> lattice. In this work, we report a simple and scalable solid-state method for Mn<sup>2+</sup> ions doping in all inorganic and hybrid organic-inorganic perovskite NCs, APbBr<sub>3</sub> (A = Cs<sup>+</sup> / CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> / CH<sub>3</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup> / CH(NH<sub>2</sub>)<sup>2+</sup>). All Mn-doped NCs show broad Mn<sup>2+</sup> emission around 600 nm along with excitonic emission, indicating the exciton to the dopant energy transfer, which facilitates the long-lived  ${}^4T_{1g} - {}^6A_{1g}$  Mn<sup>2+</sup> d-d transition. The quantum efficiency of the Mn<sup>2+</sup> emission is tuned by varying the dopant concentration and can reach well over 20%.

## Investigating the origin of dual emission in hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$

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Methylammonium lead halides ( $\text{CH}_3\text{NH}_3\text{PbX}_3$ ; X= I, Br, Cl) are one of the most promising perovskite materials for making photovoltaic devices, photodetectors, lasers and light-emitting diodes (LEDs). Thus, understanding their structural, optical and electronic properties is crucial for the development of the mentioned application/devices. We investigated structural phase transition and its importance on the radiative recombination mechanism in one of the most promising solar cell materials:  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ . UV-Visible absorption and Photoluminescence studies on polycrystalline samples revealed observation of dual peaks in methylammonium lead bromide. Further, origin of two peak structure was extensively investigated both theoretical and experimentally. Theoretical calculations predict energy landscape with appearance of two closely spaced minima with different orientations of methylammonium and an octahedral tilt in energy vs molecular orientation plot. Electronic structure of these two systems also show small shift in valence band and no shift in conduction band which is consistent with the energy difference of dual emission peaks. We hope this new finding will provide new insights into the emission properties of the hybrid perovskites.

# Charge Transport in MAPbX<sub>3</sub> Perovskite Solar Cells with Inorganic Hole Transport Materials

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## Abstract

Hole extraction layer is a major factor limiting effective charge transport in perovskite solar cells. While inorganic hole transport materials (HTM) provide ambient stability, the photovoltaic conversion efficiency of the cells is compromised. Systematic analysis of carrier concentration, mobilities and accumulation as a function of electronic band structure of the HTM relative to organolead halide perovskite layer would be beneficial for device structure optimization. Such analysis of solution-processed complex oxides of copper and nickel in p-i-n structure of perovskite solar cells is reported here. Electrochemical impedance spectroscopy and photoelectrochemistry are the principal techniques employed for in-situ and ex-citu measurements respectively. Improvement in photovoltaic performance consequent to better hole transport characteristics is also reported.

# Understanding the Growth Dynamics of Organometal Halide Perovskite ( $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ) Thin Films on $\text{SiO}_2$ and ITO Coated Glass Substrate

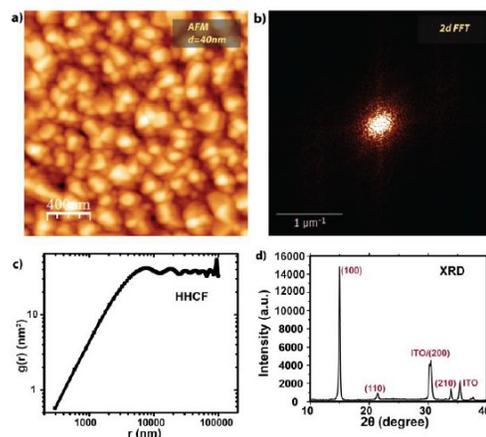
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Organometal halide perovskites semiconductors have drawn extensive attention for their breakthrough performance in many research areas in optoelectronic devices, such as solar cells, thin film transistors, lasers, LED, sensors etc. In these devices, organometal halide semiconductors serve as active layer; so the surface morphology and resulting physical properties of the thin active layer crucially dependent on the growth conditions. Hence, the knowledge of growth dynamic is of utmost importance to optimize the device performance.

$\text{CH}_3\text{NH}_3\text{PbBr}_3$  film was deposited using a co-evaporation method under high vacuum and thickness was measured by a digital thickness monitor. The evolution of surface morphology and scaling behavior of vacuum deposited  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  thin films grown on ITO-glass substrates have been studied using atomic force microscopy (AFM) and height-height correlation function (HHCF) analysis. X-ray diffraction measurement confirms the crystalline nature of the  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  thin films on atomically smooth  $\text{SiO}_2$  substrates and ITO-glass substrates at different substrate temperature and for various film thicknesses (5-40 nm). Fig. 1(a) shows the AFM image of 40-nm thick perovskite film on ITO substrate and Fig. 1(b) shows its corresponding 2D - fast Fourier transform (2D FFT) image that exhibit a ring-like structure. Figure 1(c) and (d) shows the HHCF plot and the XRD pattern of the 40nm thick perovskite film on ITO substrate. Based on the HHCF analysis, roughness exponent ( $\alpha$ ) is found to be 0.8 and 0.9 on ITO substrate and  $\text{SiO}_2$  substrate, respectively. From the 2D-FFT and the scaling exponent analysis, we conclude that the morphology evolution of  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  films is dominated by mound formation. We find that ITO substrate shows better crystallinity of the film, which can be used for device application, while  $\text{SiO}_2$  substrate gives rise to a smoother perovskite film.

Fig. 1. (a) AFM image of 40nm thin  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  film on ITO substrate and (b) the corresponding 2D FFT image of the film. (c) Height-height correlation plot and (d) XRD pattern of 40-nm-thick  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  film on ITO substrate.



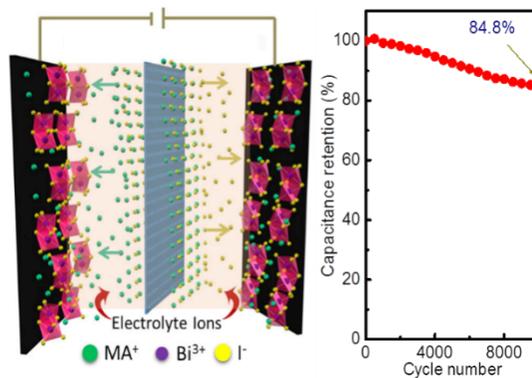
# Zero-dimensional methylammonium bismuth iodide based lead-free perovskite capacitor

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**ABSTRACT:** Development of novel, environmentally friendly and sustainable energy storage devices have attracted considerable research attention in modern times because of the rapid depletion of unsustainable fossil fuels and to satisfy the demands of the fast-growing electronic industry. Electrochemical capacitors with their long life-span, high power density, fast charge-discharge characteristics, and low-cost of production are regarded as excellent energy storage devices, as they have the potential to complement or even replace batteries in numerous applications.<sup>1</sup> The current research in this area is mainly focused on exploring novel low-cost electrode materials with higher energy and power densities.<sup>2</sup> Hybrid perovskites are emerging as an excellent candidate in this regard.<sup>3</sup> Herein, we fabricated an electrochemical double layer capacitor (EDLC) using methylammonium bismuth iodide ( $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ ), a lead-free, zero-dimensional hybrid perovskite material.<sup>4</sup> A maximum areal capacitance of  $5.5 \text{ mF/cm}^2$  was obtained and the device retained 84.8% of its initial maximum capacitance even after 10,000 charge-discharge cycles. Impedance spectroscopy measurements revealed that the active layer is providing high surface area for the electrolyte to access. As a result, the charge transport resistance is reasonably low, which is advantageous for delivering excellent performance. Details of the results will be presented.

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## Effect of Doping in Inorganic Perovskite Quantum Dots

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Metal halide perovskite nanocrystals have emerged as a class of optoelectronic materials, with excellent optical absorption and emission qualities. The most promising perovskite structures rely on lead as a cationic species, thereby hindering commercial application. In this work, we present a method to synthesize Sn based perovskite quantum dots (QDs) of CsPb<sub>1-x</sub>Sn<sub>x</sub>(Br/I)<sub>3</sub>. We have studied the colloidal stability of the QDs under different conditions and have found them to be similar to their corresponding lead based analogues. Interestingly, it has been found that doping several isovalent cations like Sn<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> in CsPbBr<sub>3</sub> nanocrystals gives rise to blueshift in the bandgap which is opposite to what is expected. Using first principle density functional theory, we have tried to explain the observed experimental trend. We have shown that effect of spin orbit coupling and lattice contraction upon doping is very crucial in understanding this effect.

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## How differently does a molecule at the A site of a hybrid perovskite behave from an atom?

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There is a strong correlation between the structure of a material and its electronic structure. This has been one of the basic trends of solid state chemistry. In inorganic perovskites of the form  $ABX_3$  where A and B are cations and X is an anion, one finds that the size of the A site cation dictates the structural distortions. These are primarily driven by steric effects. A larger atom at the A site increases the unit cell volume, that results in an increased B-X bond lengths as well as B-X-B bond angles. This two have different effects on the band gap of the system. However which effect shall dominate, depends on the relative compressibilities of the  $BX_6$  and  $AX_{12}$  polyhedras. Recently hybrid lead halide perovskite materials, where the A site is occupied by an organic molecule is showing enough promise as a solar cell material. Here we can do steric engineering to tune the optical band gap by changing the size of the A site molecule. In this work we will present our recent results using density functional theory based calculations on trying to understand how the presence of a molecule at the A site of a perovskite lattice leads to very unconventional behaviour compared to its inorganic counterpart. It is both the size of the molecule as well as its orientation in the inorganic cage formed by Pb and Br, which determine the favoured structure. At the microscopic level, the basic energetics which come into play are steric effects as well as hydrogen bonding. With a change in volume the inorganic perovskite  $CsPbBr_3$  shows systematic change in the Pb-Br and Pb-Br-Pb bond angles. However in hybrid perovskites, due to the effect of the molecule, the changes are not systematic. Also , expansion of the unit cell volume shows different form of structural distortions compared to a volume compression. We show that understanding the structural distortions as a function of volume can help us understand some of the ambiguities that exist in the published literature<sup>1,2</sup> .

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# Orientation Dependent Photophysics of 2-D Butylammonium Lead Iodide Perovskite

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2-D organic-inorganic hybrid lead halide perovskites are recently being reported to show higher stability to ambient air compared to their 3-D analogues.<sup>1,2</sup> This improved stability has motivated researchers to understand the optoelectronic properties of 2-D perovskites. Interestingly, our results show that the 2-D hybrid lead halide perovskites show orientation dependent optical properties. Such orientation dependent photophysics remains largely unexplored for these 2-D perovskites. Herein we synthesized 2-D, one-layer thick, butylammonium lead Iodide ( $\text{CH}_3(\text{CH}_2)_3\text{NH}_3$ )<sub>2</sub>PbI<sub>4</sub> perovskite and investigated their orientation dependent photoluminescence. Our preliminary results suggest that the single-crystal-like flake of the 2-D perovskite exhibits two excitonic emissions, and their relative intensity strongly depends upon angle between incident light and sample surface. Interestingly, both excitonic emissions are observed from the flake even when excited with photons with energy much lower than the bandgap, suggested significant cross-section of multi-photon absorption in our sample. This orientation dependent anisotropy in photoluminescence intensity disappears when the flake is crushed into powder or polycrystalline films. Thorough understanding of this orientation dependent photophysics of 2-D perovskite will provide new insights to optimize their optoelectronic applications.

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# Mechanochemical synthesis of stable and phase pure $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ double perovskite

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Halide double perovskites having the general chemical formula  $\text{A}_2\text{M}'(\text{I})\text{M}(\text{III})\text{X}_6$  have recently been considered as the potential candidates for photovoltaic applications. However, the materials in this category studied so far are suffering from the issue of either wide ( $> 2\text{eV}$ ) or indirect nature of the band gaps.<sup>1,2</sup> Early this year, a double perovskite  $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$  (CCSC) having a bivalent ion in place of  $\text{M}'(\text{I})$  and hence a 2-D layered structure, has been reported. It has an appropriate band gap of  $\sim 1\text{ eV}$  also found to be stable at ambient conditions.<sup>3</sup> CCSC and other double perovskites reported so far have been synthesized either by precipitation from acids or by solid state sintering method. In my poster presentation, I will discuss about the simple mechanochemical and other methods of synthesis of CCSC and its structural, optical and thermal characterization. Mechanochemical synthesis is very easy, environmental friendly and industrially scalable method to get the desired product. Also, I will discuss the reversible changes in the properties of the final product upon heating and cooling it and the effect of the polarity of the solvents on the stability of the material. Magnetic interactions and delocalization of Cu  $d^9$  electrons studied using magnetization with temperature and EPR spectroscopy will also be included.

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