

Abstracts (Invited Speakers)

Template Mediated Synthesis of Shape Controlled Hybrid Organohalide Perovskites

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Perovskite nanocrystals (NCs) are at the centre of materials research interest owing to the immense potentials in light-harvesting and light-generation applications realized within a short span. Designing shape controlled perovskite NCs in solid state remains the most demanding task considering today's wide-spread optoelectronic applications based on solid substrates. Direct conversion of pre-processed binary NCs on solid substrates into shape controlled hybrid perovskites holds prospects towards manifold device applications. We report a route for realizing shape controlled hybrid organohalide perovskite NCs from two-dimensional (2D) PbS NCs.¹ Rectangular PbI₂ NCs are first designed by iodination of PbS NCs, which are subsequently transformed into the well-defined rectangular hybrid perovskite NCs by controlled CH₃NH₃Br exposure.² Global and local structural analyses reveal transition of cubic lattice of PbS to hybrid perovskites with a mixture of cubic and tetragonal phases exhibiting a bimodal distribution of shorter Pb-Br and longer Pb-I bonding arrangements around an immediate neighboring lead absorber within first coordination shell. This direct all anion exchange reaction route is further extended for PbS nanocubes to realize shape controlled hybrid perovskites. The process opens up possibility of realizing shape controlled perovskite NCs on flexible substrates from suitable existing binary NCs.

References:

1. Ali Hossain Khan, Somnath Pal, Amit Dalui, Jayita Pradhan, D. D. Sarma, and Somobrata Acharya, *Chem. Mater.*, **2017**, 29, 1175–1182

2. Jayita Pradhan, Soham Mukherjee, Ali Hossain Khan, Amit Dalui, Biswarup Satpati, Carlo U. Segre, D. D. Sarma, and Somobrata Acharya *J. Phys. Chem. C*, **2017**, 121 , 6401–6408

Halide perovskite quantum dot solar cells

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Quantum dot (QD) sensitized solar cells emerged in 2010 as the newest technology in the NREL chart and cesium lead triiodide (CsPbI_3) happens to be the new QD leader within the promising family of organohalide and all-inorganic lead perovskite materials. While CsPbI_3 has a suitable band gap providing high photoconversion efficiencies (PCE), CsPbBr_3 has much lower efficiencies. However stability of these QDs and the fabricated devices follow the opposite trend and those with CsPbI_3 are the least stable. Focusing on a trade-off between PCE and stability, there is a tremendous scope of research on halide perovskite QD solar cells with the ultimate goal for technology transfer with large area cells. This lecture will focus on few strategies such as variation of the halide composition in CsPbX_3 ($X = \text{Br}, \text{I}$), doping transition metal, grain boundary passivation and nanosheets as alternatives to QDs. The aim of our research is to strike an optimized balance between PCE and stability of halide perovskite QD photovoltaic devices.

Solid State Chemistry with Inorganic Perovskite Halides

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Traditionally, inorganic perovskite type halides are synthesized by solution based method with the help of long chain organic capping ligands, complex organometallic precursors and high boiling organic solvents that are not only expensive but also environmentally hazardous. A simple, energy efficient and universal synthetic method to prepare inorganic halides is necessary which can produce gram-scale quantities of the materials without using hazardous solvents, complex organometallic reagents and organic capping ligands.

Mechanochemical synthesis (i.e. all-solid-state synthesis) is an attractive synthetic procedure with remarkable simplicity, rapidity, reproducibility and environmental friendly nature. We have demonstrated a room temperature, solvent-free, general, and scalable (~1g) all-solid-state mechanochemical synthesis and characterizations of different inorganic perovskite type halides with versatile structural connectivity with three (3D), two (2D) and zero (0D) dimensional structures.¹ 3D CsPbBr₃, 2D CsPb₂Br₅, 0D Cs₄PbBr₆, 3D CsPbCl₃, 2D CsPb₂Cl₅, 0D Cs₄PbCl₆, 3D CsPbI₃ and 3D RbPbI₃ with the reasonable optical properties are obtained via this all-solid-state mechanochemical grinding. The all-solid-state synthesis is materialized via an inorganic retro-synthetic approach, which directs to decide on the suitable solid-state precursors (eg. CsX and PbX₂ (X = Cl/Br/I)) with desired concentration. Moreover, we have performed post-synthetic structural transformation from 3D to 2D and 0D perovskite type halides by the same mechanochemical synthesis at room temperature. In the last part of the talk, I will demonstrate the various synthetic strategies for powder, ingot, nanoparticles and 2D nanoplates of Cs₃Bi₂I₉ and Cs₃Bi₃I₁₀; and their opto-electronic properties.

1. Provas Pal, Sujoy Saha, Ananya Banik, Arka Sarkar, and Kanishka Biswas, *Chem. Eur. J.*, 2017 (Under revision)

Accurate, Scalable Electronic Structure Description of Materials for Light Harvesting and Light Emission

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This talk describes our computational approach to materials for light harvesting and light emission, including new materials for thin-film photovoltaics (PV) and hybrid organic-inorganic perovskites with large, optically active organic functionalities and large, complex crystalline structure. High accuracy as well as scalability to large systems and on very large, parallel computers is achieved within the FHI-aims all-electron electronic structure code (the development of which is led by the author), which is based on localized, numerically tabulated atom-centered quantum-mechanical basis functions. This prescription lends itself to all-electron calculations across the periodic table for non-periodic as well as periodic system geometries, including scalar-relativistic and spin-orbit corrections and hybrid density functionals, proven up to system sizes of approximately 1,000 atoms at full all-electron accuracy. Structure and band structure predictions at this level of theory are demonstrated for a new class of multinary I₂-II-IV-IV₄ semiconductors for PV, based on I=Cu/Ag, II=Ba/Sr, IV=Ge/Sn and VI=S/Se. Early prototype PV devices created in David Mitzi's group show efficiencies above 5%. We then show how the same underlying theoretical approach allows us to rationalize energy band alignments and luminescence properties of layered perovskites based on PbX₄⁻ (X=Cl/Br/I) inorganic and oligothiophene-derived cationic organic components. We finally comment on broader materials-centric activities at Duke University and in North Carolina's Research Triangle region, including a new materials database "Hybrid³" that will focus on organic-inorganic Perovskite materials.

Photo-physical Model for Long-lived Non-Exponential Relaxation Dynamics in Hybrid Perovskite Semiconductors: Beyond Photon Recycling

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Abstract

Hybrid Perovskites semiconductors have shown tremendously unrealistic positive progress in the area of solar cells community. Though, early demonstration by Mitzi et al using lower dimension, i.e., 2D hybrid perovskite devices already hinted use of these materials for optoelectronics [1], which was re-triggered by Miyasaka et al by exploring 3D hybrid perovskites in mesoscopic solar cells. [2] Since then there is a rapid progress in this field. While improving the performance of devices, researchers also realized there are challenges in handling these materials, which needs to be addressed to ensure the deployment of them for consumer applications. Our research group has been working on fundamental aspects of these materials [3] along with early demonstration of room temperature electroluminescent diode from blue to NIR range. [4,5]

In this talk, I shall like to focus on some of recent findings about defects dynamics in perovskite semiconductors. This work was motivated by on-going debate in community about long-lived photoluminescence lifetime, where photo-recycling, Rashba-splitting vs trapping based models have been proposed to explain red-shifted long-lived component observed by many groups. We developed a classical donor-acceptor based model, borrowed from nitrogen dopant in GaP semiconductors and in many inorganic semiconductor materials to explain long-lived (> 10s ns) non-exponential relaxation dynamics in hybrid perovskites semiconductor single crystal as a function of fluence power, emission wavelength and halide ion. We conclude that bromine based system has got wider energy distribution of defects states than iodine crystal, however, the over-all trap-density is higher in iodine based crystal.

References:

- [1] Chondroudis, K.; Mitzi, D. B. *Chem. Mater.* 1999, 11, 3028– 3030.
- [2] Kojima, A.; Teshima, K; Shirai, Y; Miyasaka. T *J. Am. Chem. Soc.*, **2009**, 131 (17), pp 6050–6051
- [3] S. Singh, C. Li, F. Panzer, K. L. Narasimhan, A. Graeser, T. Gujar, A. Kohler, T. Mukundan, S. Huettner and D. Kabra *J. Phys. Chem. Lett.* Vol. 7, pp- 3014 (2016)
- [4] N. K. Kumawat, N. Jain, A. Dey, K. L. Narasimhan and D. Kabra *Adv. Func. Mater.* Vol. 27, p – 1603219 (2017)
- [5] N. K. Kumawat, D. Gupta and D. Kabra *Energy Tech.* Vol. 5, p-1734 (2017)

Lead Halide Perovskites for Next Generation Photovoltaics

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Metal halide perovskites have drawn significant attention in recent years because of its ability to deliver high efficiency solar cells.^{1,2} Efforts are now being directed towards the design tandem solar cells to boost the efficiency beyond single crystal silicon solar cells.³ However, barriers to transform laboratory scale devices to large scale commercial technology remain. Unusual excited state properties of these materials are also creating new opportunities to explore optoelectronic applications.

Mixed halide lead perovskites with continuous tuning of the semiconductor bandgap are regarded as possible candidates for such applications.^{3,4} By varying the halide ion composition of methylammonium lead iodide/bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_x\text{I}_{3-x}$ ($x=0$ to 3)) it is possible to tune the bandgap between 1.55 eV and 2.43 eV. In addition to photovoltaic applications these mixed halide perovskites offer rich photophysical properties with applications in lasing and optoelectronic devices. An intriguing property of mixed halide lead perovskites (e.g., $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$) is phase segregation to create iodide-rich and bromide-rich regions under visible irradiation.^{5,6} The halide ion movement in mixed halide films can be tracked from the changes in the photoluminescence and absorption spectra. Photoinduced segregation in mixed halide perovskite has a direct influence on decreasing the solar cell efficiency as segregated I-rich domains serve as charge recombination centers. The recovery of loss in the external quantum efficiency mirrors the dark recovery of the absorption showing the reversibility of the photoinduced halide segregation. Implication of such halide ion migration in mixed halide perovskite solar cell will be discussed.

Related Readings

1. Manser, J. S.; Saidaminov, M. I.; Christians, J. A.; Bakr, O. M.; Kamat, P. V., Making and Breaking of Lead Halide Perovskites. *Accounts of Chemical Research* **2016**, *49*, 330-338.
2. Manser, J. S.; Christians, J. A.; Kamat, P. V. Intriguing Optoelectronic Properties of Metal Halide Perovskites. *Chem. Rev.* 2016, *116*, 12956–13008.
3. Kamat, P. V., Hybrid Perovskites for Multijunction Tandem Solar Cells and Solar Fuels. A Virtual Issue. *ACS Energy Lett.*, 2018, *3*, 28-29
4. Hoffman, J. B.; Schleper, A. L.; Kamat, P. V., Transformation of Sintered CsPbBr_3 Nanocrystals to Cubic CsPbI_3 and Gradient $\text{CsPbBr}_x\text{I}_{3-x}$ through Halide Exchange. *J. Am. Chem. Soc.* **2016**, *138*, 8603–8611.
5. Draguta, S.; Sharia, O.; Yoon, S. J.; Brennan, M. C.; Morozov, Y. V.; Manser, J. M.; Kamat, P. V.; Schneider, W. F.; Kuno, M. Rationalizing the light-induced phase separation of mixed halide organic-inorganic perovskites. *Nat. Commun.* 2017, *8*, Article No. 200 (DOI: 210.1038/s41467-41017-00284-41462).
6. Yoon, S. J.; Kuno, M.; Kamat, P. V. Shift Happens. How Halide Ion Defects Influence Photoinduced Segregation in Mixed Halide Perovskites. *ACS Energy Lett.* 2017, 1507-1514.

Atomic Models for Surface Stabilization of Cesium Lead Halide Perovskite Colloidal Quantum Dots

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Cesium lead halide perovskite colloidal quantum dots (CQDs) have been emerged as promising optoelectronic materials due to their unique optical properties and low-temperature solution processability. Despite the advantages, structural instability of the perovskite CQDs leads to size and shape changes as well as phase transition, resulting in uncontrollable physicochemical properties. Recent synthetic approach using metal halides made great progress on enhancing structural stability of the CQDs [1]. However, the influence of the additional metal halides on the perovskite CQDs, especially on their surfaces, is not fully understood. We formulate atomic models of perovskite surfaces for microscopic understandings on surface chemistry of the perovskite CQDs in the presence of the metal halides. Based on electron counting models and first-principles DFT calculations, we found various ligand-passivated surfaces of the CQDs strongly affected by chemical reactions that depend on the additional metal halides. From thermodynamic comparisons of our atomic models, we deduced that amine-halide surfaces could be greatly stabilized with the presence of the metal halides. Our results also account for the recent experimental observations on improving structural stability of the perovskite CQDs. [1] J. Y. Woo et al. *Chem. Mater.* 29, 7088 (2017)

Efficient Exciton to Dopant Energy Transfer in Mn²⁺ Doped (C₄H₉NH₃)₂PbBr₄ 2D Layered Perovskites

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Abstract:

Three dimensional ABX₃ perovskite material has attracted immense interest and applications in optoelectronic devices due to their enabling properties. Recently, Mn²⁺ doping *directly* into APbCl₃ type 3D nanocrystals, manifesting host to dopant energy transfer, have been reported for LED display applications. Strongly bound excitons in the doped system can enhance the dopant-carrier exchange interactions leading to efficient energy transfer. Here, we report simple and scalable synthesis of Mn²⁺ doped (C₄H₉NH₃)₂PbBr₄ 2D layered perovskites. The Mn²⁺ doped 2D perovskite shows enhanced energy transfer efficiency from the strongly bound excitons of the host material to the *d* electrons of Mn²⁺ ions resulting in intense orange-yellow emission due to spin forbidden internal transition (⁴T₁ → ⁶A₁) with the highest quantum yield (Mn²⁺) of 37%. Owing to this high quantum yield, stability in ambient atmosphere, simplicity and scalability of the synthetic procedure, Mn²⁺ doped 2D perovskites could be beneficial as color converting phosphor material and as energy down-shift coating for perovskite solar cells. The newly developed Mn²⁺ doped 2D perovskites can be a suitable material to tune dopant-exciton exchange interactions to further explore their magneto-optoelectronic properties.

Hybrid Perovskites under pressure – revisiting some structural chemistry concepts

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Inorganic perovskites of the form ABX_3 have been studied for several decades now, and few rules have emerged of how the perovskite will behave under pressure (chemical as well as hydrostatic). A smaller atom at the A site results in a smaller unit cell volume being favoured. This leads to a decrease in the B-X bondlengths. However, this results in an enhanced Coulomb interaction between electrons on the B site and the anion. The system then responds by rotating the BX_6 octahedra so that the B-X-B angles deviate from 180° that one would find in an ideal perovskite unit cell. These structural distortions turn out to have opposite tendencies in modifying the band gap of the system. While a decrease in the B-X bondlengths results in a reduction in the band gap, the angular distortions lead to an enhancement of the band gap. So, indeed the question is which effect would prevail. This again has been well answered in the context of inorganic perovskites, and the relative compressibilities of the AX_{12} unit as against the BX_6 unit determine the nature of structural distortions which would prevail. Our earlier work[1] where the atom at the A site considered were CH_3NH_3 and $C_2H_5NH_3$ showed that the larger molecule led to an increase in the band gap. This led us to the question of whether this was a generic trend. Carrying out systematic studies of the changes in the structural as well as electronic properties as a function of the volume led systematics which were different from what one knew in the context of inorganic perovskites and this will be the subject of this talk.

1. M. Mittal, A. Jana, S. Sarkar, Priya Mahadevan, J. Phys. Chem. Lett. 7, 3270 (2016); S. Sarkar and Priya Mahadevan, Phys. Rev. B 95, 214118 (2017).

Uses of Hybrid Coordination Polymers as Chemosensors

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Among the various sensing methods, luminescence based methods have gained much attention in recent years due to their advantageous features such as easy way of manipulation, high sensitivity, and real-time monitoring with rapid response time. Hybrid Coordination Polymers (HCPs) are relatively a new class of hybrid crystalline materials with diverse structural characteristics and tunable pore size constructed by the connectivity of metal ions or metal clusters and organic ligands. Recently, significant progress has been made in the uses of the luminescence property of HCPs for sensing of pH, small molecules, metal ions and explosives. Generally the diverse pore topologies and functional sites make HCPs as suitable sensory materials through the molecular level interactions between the framework of HCPs and the analytes. In this presentation, our recent research work based on sensing of hazardous chemicals such as nitro-explosives, pesticides and metal ions in liquid medium would be described and discussed [1-7].

References:

1. Mahata, P.; S. K. Mondal; Singha, D. K.; Majee, P. *Dalton Trans.*, **2017**, 46, 301.
2. Singha, D. K.; Majee, P.; Mondal, S. K.; Mahata, P. *ChemistrySelect*, **2017**, 2, 5760..
3. Singha, D. K.; Majee, P.; Mondal, S. K.; Mahata, P. *ChemistrySelect*, **2017**, 2, 3388.
4. Singha, D. K.; Mahata, P. *Inorg.Chem.*, **2015**, 54, 6373.
5. Singha, D. K.; Majee, P.; Mondal, S.K.; Mahata, P. *RSC Adv.*, **2015**, 5, 102076.
6. Singha, D. K.; Majee, P.; Mondal, S.K.; Mahata, P. *Eur. J. Inorg. Chem.*, **2015**, 1390.
7. Singha, D. K.; Bhattacharya, S.; Majee, P.; Mondal, S. K.; Kumar, M.; Mahata, P. *J. Mater. Chem. A*, **2014**, 2, 20908.

Carrier dynamics in CsPbBr₃ perovskite nanocrystals from time-resolved THz spectroscopy

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Colloidal all inorganic CsPbX₃ (X = Cl, Br, I) perovskite nanocrystals (NCs) have emerged to be an excellent material for applications in light emission, photovoltaics, and photocatalysis. We have used time-resolved THz spectroscopy to study the detailed dynamics of photo-generated carriers in 11 nm sized colloidal CsPbBr₃ NCs. Our results established a three-fold carrier recombination mechanism, namely, non-radiative Auger, bi-molecular electron-hole recombination and inefficient trap-assisted recombination in. We observed a negligible influence of surface defects in trapping charge carriers, which, in turn, results in to desirable intrinsic transport properties, from the perspective of device applications, such as remarkably high carrier mobility ($\sim 4500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), large diffusion length ($> 9.2 \mu\text{m}$) and high luminescence quantum yield (80%). In thin films (few microns thick) of the NCs, the carrier dynamics changes rather significantly which leads to a decrease in carrier mobility by almost an order, most likely due to inherent disorder and/or large to intermediate polaron formation. Carrier dynamics is slow in case of two-photon pumping compared to that with single photon absorption probably due to different initial excited states involved in these processes. Auger recombination is apparently absent under two-photon excitation condition. We also have measured the kinetics of photogenerated electron and hole transfer processes in CsPbBr₃ NCs in presence of benzoquinone (BQ) and phenothiazine (PTZ) molecules as electron and hole acceptors, respectively. Efficient hot electron/hole transfer with a sub-300 fs timescale is the major channel of carrier transfer, thus overcomes the problem related to Auger recombination. A secondary transfer of thermalized carriers also takes place with time scales of 20-50 ps for electrons and 137-166 ps for holes. This work suggests that suitable interfaces of CsPbX₃ NCs with electron and hole transport layers would harvest hot carriers, increasing the photovoltaic and photocatalytic efficiencies.

Halide Perovskites: Structural Diversity and Opportunities for Semiconductor Design/Fabrication

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Although known for more than a century, organic-inorganic hybrid and related inorganic halide-based perovskites have received extraordinary attention recently, because of the unique physical properties of the lead(II)-based systems, which make them outstanding candidates for application in photovoltaic (PV) and related electronic devices. Despite the high levels of device performance, incorporation of the heavy metal lead, coupled with issues of device stability and electrical hysteresis pose challenges for commercializing these exciting technologies. This talk will explore beyond the current focus on three-dimensional (3-D) lead(II) halide perovskites (e.g., $\text{CH}_3\text{NH}_3\text{PbI}_3$), to highlight the great chemical flexibility and outstanding potential (and challenges) of the broader 3-D and lower-dimensional perovskite family. As part of the discussion, the prospects for replacing lead with other metals, the importance of structural dimensionality for determining semiconducting character, along with the promise for both inorganic and organic structural components to play an active role in determining the overall hybrid semiconducting character, will be emphasized. Beyond structural flexibility, as time allows, the talk will further discuss how chemical flexibility leads to an unusually large range of processing options for preparing high-performance perovskite films. Outstanding functionality combined with versatile/facile processing provide two pillars for future application of this materials family.

Beyond Colloidal Pb-Halide Perovskite Nanocrystals

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Pb-halide perovskites exhibit defect-tolerant behaviour resulting into efficient optoelectronic properties. In last two years, we have worked on various aspects of material design, optical and optoelectronic properties of colloidal cesium lead halide perovskite nanocrystals.¹⁻⁵ The key aspects that make Pb-halides an unique class of optoelectronic materials are: (i) Pb^{2+} exhibit stable $n\text{S}^2$ electronic configuration in the outermost orbital, (ii) small effective masses of charge carriers because of 3-D structural network of $[\text{PbI}_6]^{4-}$ octahedral with Pb-I-Pb bond angles close 180° , and (iii) strong spin-orbit splitting of Pb 6p states (conduction band minimum).

From last one year, we have started searching for Pb-free metal halide nanocrystals that has the potential to exhibit the combination of these three properties.⁶⁻⁸ In this talk, I will discuss about our experiences on Pb-free metal halide nanocrystals. The Pb-free materials that will be discussed are colloidal thallium halide (TlX), cesium antimony halide ($\text{M}_3\text{Sb}_2\text{X}_9$; M = Cs and Rb), and cesium bismuth halide ($\text{Cs}_3\text{Bi}_2\text{X}_9$) nanocrystals, where X signifies halides. Intrinsic issues regarding material design and photophysical properties relevant for optoelectronic applications will be discussed.

References:

1. Swarnkar, A.; Chulliyil, R.; Ravi, V. K.; Irfanullah, M.; Chowdhury, A.; Nag A. *Angew. Chem. Int. Ed.* **2015**, 53, 15424.
2. Yettapu, G. R.; Talukdar, D.; Sarkar, S.; Swarnkar, A.; Nag, A.; Ghosh, P.; Mandal, P. *Nano Lett.* **2016**, 16, 4838.
3. Ravi, V. K.; Markad, G. B.; Nag, A. *ACS Energy Lett.* **2016**, 1, 665.
4. Mir, W. J.; Jagadeeswarara, M.; Das, S.; Nag, A. *ACS Energy Lett.*, **2017**, 2, 537.
5. Sarkar, S.; Ravi, V. K.; Banerjee, S.; Yettapu, G. R.; Markad, G. B.; Nag, A.; Mandal, P. *Nano Lett.*, **2017**, DOI: 10.1021/acs.nanolett.7b02003.
6. Swarnkar, A.; Ravi, V. K.; Nag, A. *ACS Energy Lett.*, **2017**, 2, 1089.
7. Mir, W. J.; A. Warankar, A.; Acharya, A.; Mandal, P.; Nag, A. *Chem. Sci.* **2017**, 8, 4602.
8. Pal, J.; Manna, S.; Mondal, A.; Das, S.; Adarsh, K,V.; Nag A. *Angew. Chem. Int. Ed.* **2017**, 56, 14187.

Exciton Migration and Trapping in Hybrid Perovskite Materials

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Organometal halide perovskite materials exhibit excellent optical and electronic properties, which make them suitable for advanced device applications. The success of three-dimensional bulk perovskites created great research interest in zero-dimensional, two-dimensional and perovskite based colloidal nanocrystals (PNCs). During the short span of time, these new materials showed great promise in several applications such as solar cells, light emitting diodes, lasers, photodetectors, memories and sensors. Recent studies suggest that the electrical and optical properties of these nanostructures are superior to traditional semiconducting inorganic quantum dots. Nevertheless, the underlying photophysics of these materials still not well understood. A better and in-depth understanding of the photophysical properties is absolutely necessary for the further development in this area as well as to push the present efficiency limits of perovskite based optoelectronic devices. In this context, recently we have studied the excitation energy migration and electron transfer properties of hybrid PNCs. Similar to natural photosynthetic systems, these materials exhibit efficient excitation energy migration. Studies proved that the exciton migration can be channelled into electron transfer through the incorporation of suitable acceptors in the medium. On the other hand, our studies with a lead-free two-dimensional perovskite material showed the formation of self-trapped excitons due to strong electron-phonon coupling. Details of the studies will be discussed.

References:

1. C. Muthu, S. R. Nagamma, V. C. Nair, *RSC Adv.* **2014**, *4*, 55908.
2. C. Muthu, S. Agarwal, A. Vijayan, P. Hazra, K. B. Jinesh, V. C. Nair, *Adv. Mater. Interfaces* **2016**, *3*, 1600092.
3. V. C. Nair, C. Muthu, A. L. Rogach, R. Kohara, V. Biju, *Angew. Chem. Int. Ed.* **2017**, *56*, 1214.
4. C. Muthu, A. Vijayan, V. C. Nair, *Chem. Asian J.* **2017**, *12*, 988.

5. J. K. Pious, M. L. Lekshmi, C. Muthu, R. B. Rakhi, V. C. Nair, *ACS Omega* **2017**, 2, 5798.

"Techniques to Predict Reliability and Follow Degradation in Hybrid Perovskite Solar Cells"

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We present a range of methods and techniques to examine and probe perovskite solar cells. We report a clear correlation of the features observed in photocurrent noise-fluctuations to the performance parameters of hybrid perovskite solar cells. The general trend of increasing noise amplitude which spreads over a wider range of frequency as a function of aging is established. High-resolution spatial mapping of the photocurrent in typical devices and the associated variation of the noise spectrum confirms the underlying trend.

Synthetic engineering of the dimensionality and properties of hybrid perovskite systems in search of novel functionalities and applications

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Hybrid perovskite systems have attracted great attention lately in view of their unique and tunable optical and optoelectronic properties, and their applicability in high efficiency solar cell architectures. With growing insights into the processing methods and properties of these materials revealed by recent research, it is fairly well established that these systems are quite amenable to facile molecular and dopant related engineering and synthetic manipulations. These can lead to interesting forms including low dimensional ones, with interesting and tunable properties. In this talk I will present and discuss some of our recent research results in this field, highlighting some novel device related opportunities. The specifics will include *in situ* molecular control of the microstructure and its consequences for highly enhanced photoluminescence of interest to LED application, changes in the dimensionality via small molecule incorporations and the corresponding consequences for white luminescence and new charge storage application, and molecular anion doping effects in hybrid perovskites.

References: ChemSusChem, 2017, 10, 3722, J. Mater. Chem. A, 2017, 5, 18634, Adv. Mater. Interfaces, 2017, 4, 1700562, J. Appl. Phys. 2017, 121, 133107, J. Phys. Chem. Lett. 2016, 7, 4757, ACS Appl. Mater. & Interfaces, 2016, 8, 854, ChemComm, 2014, 50, 9741.

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Perovskite Solar Cell: Performance, Stability and Future Prospects

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The energy costs associated with separating tightly bound excitons (photoinduced electron-hole pairs) and extracting free charges from highly disordered low-mobility networks represent fundamental losses for many low-cost photovoltaic technologies. A low-cost, solution-processable solar cell, based on a highly crystalline perovskite absorber with intense visible to near-infrared absorptivity, that has achieved power conversion efficiency of 20 % so far in a single-junction device under simulated full sunlight.

To attain reproducibility in the performance one of the critical factors is the processing conditions of the perovskite film, which directly influences the photo-physical properties and hence the device performance. However, future response of this technology shall be determined by its inherent stability and overall cost associated with energy generation.

Perovskite Nanocrystals in Reaction Flask: Some Exciting and Some Puzzling Chemistry

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Light emitting Lead halide perovskite nanocrystals are recently emerged as a new class of functional materials for their unprecedented high emission intensity. These are ionic crystals and unlike traditional quantum dots, these do not follow the classical nucleation and growth mechanism. Their formation chemistry in reaction flask is interesting and exciting, where for each set of nanocrystals or for every size or shape, a new reaction is required. This talk will present the formation chemistry of all inorganic perovskite nanocrystals emitters in reaction flask at various reaction temperatures. In addition, doping Mn, how the photo-recombination process changes would also be discussed.

The science in perovskites from synthesis to change in materials properties is indeed exciting. In our laboratory, we were initially reluctant to start this work; but once initiated, our full strength went to this exciting field. Unless one observe, the beauty of these fabulous materials cannot be enjoyed. This talk would also reflect the instant feeling of a chemist mind while carrying out the reactions and finding new observations and new chemistry of these nanocrystals in reaction flask.

Internal Heterostructure of Pure and Anion Exchanged Cesium Lead Halide Nanocubes

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All inorganic cesium lead halide (CsPbX₃, X = Cl, Br, and I) perovskite nanocubes (NCs) exhibit fascinating optical and optoelectronic properties [1, 2]. Post-synthesis anion exchange by mixing NCs with reactive anion species have emerged as a unique capability of CsPbX₃ perovskite NCs to fine control their composition and bandgap. Understanding such anion exchange reactions is essential for both fundamental understanding and optimized applications. However, the internal structure of the anion exchanged NCs are not probed. It is largely believed that the anion exchanged NCs possess a homogeneous composition.

In this talk, we will first discuss about the surface of CsPbBr₃ NCs and the internal heterostructure that exists inside the anion exchanged CsPbX₃ (X = Br/I, and I) NCs probed by variable energy hard X-ray photoelectron spectroscopy. Our results show that for pure CsPbBr₃ NCs, there is an excess of bromide ion on the surface of the NCs. We further probed how the ligands replace the Cs⁺ ions from the surface of the NCs to stabilize the system. Whereas the anion exchange process makes the CsPbX₃ NCs as a gradient alloy with higher concentration of the exchanged anion at the surface of the NCs. A significant amount of native anions are present at the core of the NCs even optical studies suggest a complete anion conversion. The insights from this study provide important directions in future understanding about the electronic properties of the anion exchanged CsPbX₃ NCs.

Reference:

- [1] A. Swarnakar, et al, *Angew. Chem., Int. Ed.* 54, 15424 (2015)
- [2] V. K. Ravi et al, *J. Phys. Chem. Lett.* 8, 4988 (2017)
- [3] A. Haque, et al., *Submitted.*

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Perovskite nanocrystals using the solid state route

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Since 2009 there has been a renewed interest in $APbX_3$ perovskite materials due to their phenomenal achievement in the area of solar photovoltaics. Moreover, the perovskite nanomaterials too show a promise as light emitting materials along with photovoltaics. An easy method of production of perovskite nanomaterials achieved using a mortar-pestle approach will be discussed.¹ This solvent-less method does not involve any heating of the starting materials and can also be used for production of large quantities of the nanomaterials. Further, we have also used the method for doping Mn in the $APbBr_3$ nanoparticles,² which till now has been reported to be possible using only indirect methods.

1. *Solvent-free, mechanochemical syntheses of bulk trihalide perovskites and their nanoparticles*
A. Jana, M. Mittal, A. Singla, S. Sapra
Chem. Commun. 53, 3046 (2017)
2. *Doping Mn^{2+} Ions in $APbBr_3$ Perovskite Nanocrystals: Solid is the Solution*, M. Mittal, A. Jana, S. Yadav, M. S. Hassan, A. Chakrabarty and S. Sapra
(submitted)

Organic-inorganic hybrid perovskite materials for photovoltaic applications

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It has been recently discovered that a class of materials based on organic-inorganic hybrid methyl ammonium (MA) lead halides (MAPbX_3 , with $X = \text{I, Br, and Cl}$) compounds can have extraordinary photovoltaic properties, with efficiencies reaching beyond 20%. In addition, these materials also have many other attractive features, such as solution processability. While a large part of the international effort is aimed at further improving the efficiency or to improve other technological aspects, such as the stability or to replace toxic Pb, there is also an intense effort in understanding the intrinsic properties of these compounds. Curiously enough, there does not appear to be any universally accepted understanding of even the most basic properties of these materials. For example, an intensely debated issue concerns the ability of permanent dipoles on organic moieties to give rise to polar fields, either in the normal state (as in any ferroelectric material) or in the photo-excited state, contributing to its spectacular photovoltaic properties. Even estimates of the excitonic binding energy in these materials have proven to be controversial with various estimates differing by more than an order of magnitude. I shall discuss our own efforts with MAPbX_3 to understand physical properties of several of these hybrid materials. We use various techniques that are differently sensitive to the polar nature of any given material, probing time-scales from the static down to a few hundred femto-seconds, both without and in presence of photo-excitation to address several outstanding issues.

Relevant references from our work:

1. Menno Bokdam, Tobias Sander, Alessandro Stroppa, Silvia Picozzi, D.D. Sarma, Cesare Franchini, and Georg Kresse, *Sci. Rep.* 2016, **6**, 28618.
2. J Lahnsteiner, G Kresse, A Kumar, D. D. Sarma, C Franchini, and M Bokdam, *Phys. Rev. B* 2016, **94**, 214114.
3. Sharada G *et al.*, *J. Phys. Chem. Lett.* 2016, **7**, 2412.
4. Sharada Govinda *et al.*, *J. Phys. Chem. Lett.* 2017, **8**, 4113.
5. Sharada Govinda *et al.*, Unpublished