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Optoelectronic Insights into Lead-Free Metal Halide Perovskites

Background

Optoelectronic materials, crucial for present and future technologies, have long intrigued physicists, chemists, and engineers. Quantum dots, representing quantum-confined semiconductor nanostructures, were recognized with the 2023 Nobel Prize in Chemistry for Bawendi, Brus, and Ekimov. [1]. Metal halide perovskites, emerging three decades later, gained attention with Miyasaka's perovskite solar cells in 2009 [2]. Advancing the field, the colloidal synthesis of multicolor light-emitting metal halide perovskite nanocrystals in 2015 via the hot-injection method enabled diverse shapes, sizes, and compositions, making them solution processable and promising for various device applications [3].

3-dimensional (3D) metal halide perovskites, denoted as ABX_3 (A= $(CH_3NH_3)^+$, $(CHNH_2)NH_2^+$, Cs^+, or Rb^+; B= Pb^{2+}, Sn^{2+}, or Ge^{2+}; and X= Cl, Br, or I), offer adjustable light absorption and emission within the UV-visible-near infrared (NIR) range [3, 4]. Particularly, Pb-based ABX_3 perovskites hold potential for applications in photovoltaics, LEDs, and lasers [4]. Ongoing investigations explore structural variations like 2D Ruddlesden-Popper or Dion-Jacobson structures [5]. However, the toxicity of Pb limits their usage, prompting the exploration of Pb-free alternatives with promising optoelectronic properties. Bi-based vacancy-ordered perovskites, Sn-based 2D perovskites, and In-based double perovskites are considered as viable alternatives in this context [6–8].

Exemplar from contemporary research

Vacancy ordered $Cs_3Bi_2I_9$, a stable lead-free alternative in metal halide perovskite family, is synthesized into nanosheets through the hot-injection method and shape-selective re-precipitation [6]. Figure 1A shows the transmission electron microscopy (TEM) image of $Cs_3Bi_2I_9$ nanosheets. Structurally, $Cs_3Bi_2I_9$ comprises isolated 0D $(Bi_2I_9)^{3-}$ dimers created by face-sharing bismuth iodide octahedra, surrounded by Cs^+ cations (Figure 1B). These nanosheets exhibit a sharp absorption peak in the visible range due to strong exciton confinement in the isolated dimers and a broad absorption onset from an indirect bandgap and surface defects (Figure 1C). Despite the indirect bandgap causing phonon-mediated relaxation of excitons, leading to reduced radiative recombination, broadband cathodoluminescence occurs from defect-related charge carrier recombination (Figure 1D). The slow hot carrier cooling (30–70 ps) resulting from strong electron-phonon interaction offers potential benefits for energy conversion efficiencies [6]. However, limitations include non-luminescence, restricting application in light-emitting devices, and strongly localized excitons hindering carrier diffusion, affecting performance in solar cells compared to Pb-based counterparts [6, 9].
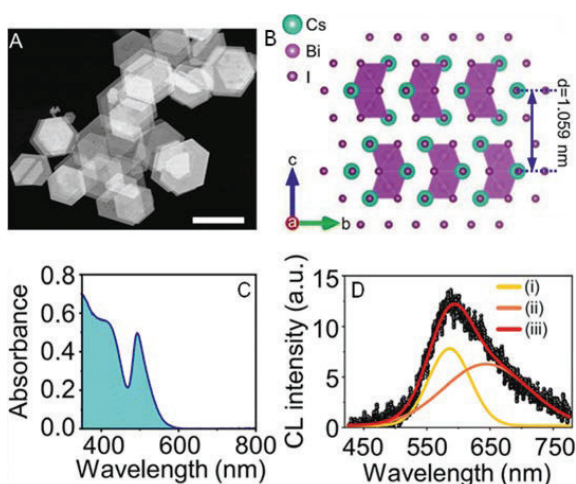
Sn-based 2D Ruddlesden-Popper metal halides present luminescent alternatives to Pb-based perovskites [7]. In these structures, an inorganic metal halide octahedral layer, conductive in nature, is sandwiched between insulating layers of organic ammonium cation spacers, forming a quantum well [5, 7]. This configuration confines charge carriers within the inorganic layers, exhibiting strong quantum and dielectric confinement. Unlike vacancy-ordered $Cs_3Bi_2I_9$ perovskites, excitons in 2D Ruddlesden-Popper structures can diffuse in-plane along the inorganic metal halide octahedral layers, making them more efficient in solar cells [5, 7]. Additionally, the soft lattice in 2D metal halide structures can be deformed by strongly bound excitons, creating a potential well where the

Fig. 1: Structural and optical properties of vacancy-ordered $Cs_3Bi_2I_9$ nanosheets. (A) Transmission electron microscopy (TEM) image of $Cs_3Bi_2I_9$ nanosheets. (B) Supercell crystal structure of $Cs_3Bi_2I_9$ perovskites with d-spacing of 1.059 nm along (002) plane. (C) UV-visible absorption spectrum and (D) cathodoluminescence (CL) spectrum of $Cs_3Bi_2I_9$ nanosheets. The CL spectrum (iii) is deconvoluted showing the luminescence contribution from band-edge recombination (i) and defect-related recombination (ii). Reproduced with permission from ref. 6. ©Royal Society of Chemistry.

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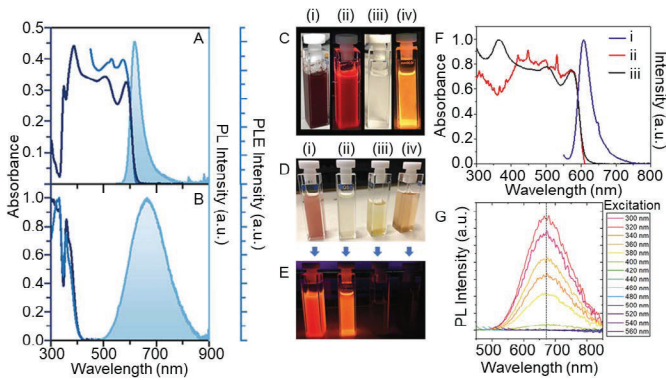sushant.ghimire@lmu.de

Fig. 2: Optoelectronic properties of alkylammonium tin iodide nanosheets without and with self-trapping of excitons. (A, B) Absorption, PL and PL excitation spectra of octylammonium tin iodide nanosheets. (C) Photographs of as-synthesized (i-ii) red-emitting and (iii-iv) broadband orange-emitting octylammonium tin iodide nanosheet suspensions in hexane at (i, iii) room light and (ii, iv) UV light. (D-E) Photographs of red-emitting and broadband orange-emitting dilute colloidal solution of octylammonium tin iodide nanosheets in hexane in (D) room light and (E) UV light after 180 min of storage in dark or exposed to light. (i) Stored in dark, (ii) washed with hexane and stored in dark, (iii) exposed to room light, and (iv) exposed to UV light. (F) PL (i), PL excitation (ii), and absorption (iii) spectra of tetradecylammonium tin iodide nanosheets. (G) Excitation wavelength-dependent PL spectra of broadband orange-emitting octylammonium tin iodide nanosheets. Reproduced with permission from ref. 7. ©American Chemical Society.

exciton is self-trapped [7]. Despite inducing broadband and significantly Stokes-shifted emission, self-trapping enhances emission quantum yield, and the broad PL is advantageous for generating white LEDs. However, achieving high quantum yield broadband white light emission at room temperature faces challenges due to thermal detrapping of self-trapped excitons (STEs) in 2D metal halide perovskites [10]. Figure 2 compares the optoelectronic properties of 2D octylammonium tin iodide nanosheets and tetradecylammonium tin iodide nanosheets synthesized via the hot-injection method, both with and without exciton self-trapping at room temperature [7].

The octylammonium tin iodide nanosheet without STEs exhibits a distinct red band-edge emission with a narrow PL spectrum (Figure 2A). This spectrum aligns closely with absorption or PL excitation (PLE) spectra, revealing a small Stokes shift. The nanosheet suspension appears red under both, room light and UV light (Figure 2C i-ii), indicating a narrow optical bandgap. Conversely, the sample with STEs in Figure 2B displays broadband emission with a significant Stokes shift and a UV optical bandgap, appearing white under room light (Figure 2C iii) and emitting orange light under UV excitation (Figure 2C iv). Broadband emitting samples exhibit PL lifetimes in the order of several hundreds of ns to μs, indicating strongly trapped exciton formation [7]. The orange-emitting nanosheets show no change in PL maxima or PL bandwidth when excited at different wavelengths (Figure 2G), indicating the absence of defect-related emissive states within the bandgap. The broad emission stems from STEs influenced by octahedral distortion and structural reconstruction in Sn-based 2D Ruddlesden-Popper structures [7]. In contrast, nanosheets with long-chain organic cations like tetradecylammonium tin iodide exhibit minimal octahedral distortion and enhanced structural stability, displaying sharp band-edge emission (Figure 2F). Structural reconstruction in short-chain octylammonium-based tin iodide nanosheets lead to the formation of 0D tin iodide clusters with a high PL quan-

tum yield. For instance, the PL quantum yield for red-emitting nanosheets is <1 %, while the broadband orange-emitting sample with STEs has a 25 % PL quantum yield [7]. Despite these properties, the stability of Sn-based metal halide perovskites under ambient conditions is challenging (Figure 2D-E), emphasizing the need for stable alternatives. Recent advancements introduce Hafnium and Zirconium halide-based octahedral clusters as promising, stable, and lead-free alternatives with near-unity PL quantum yield in the visible region [11].
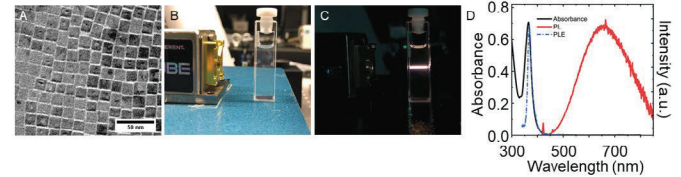

Fig. 3: Bi³⁺-doped $Cs_2AgInCl_6$ double perovskite nanocrystals as alternative broadband emitters. (A) TEM image of the nanocrystals. (B-C) Photographs of nanocrystal colloidal solution under (B) room light and (C) 375 nm laser excitation. (D) Absorbance (black), PL (red), and PLE (blue) spectra of the nanocrystal colloidal solution. The excitation wavelength is 375 nm. These experiments were performed at the Institute of Physics, University of Rostock in collaboration with Prof. Christian Klinke. The images copyright belongs to Dr. Sushant Ghimire.

Metal ion-doped double perovskites are emerging as promising broadband emitters for white LEDs, potentially surpassing Sn-based or Bi-based alternatives in terms of stability and photoluminescence [8, 12]. They have demonstrated a PL quantum yield of nearly 100% [8]. Figure 3 illustrates an example of colloidal $Cs_2AgInCl_6$ double perovskite nanocrystals, synthesized via the hot-injection method, displaying broadband emission upon Bi³⁺ doping. The origin of the broadband emission in Bi³⁺-doped $Cs_2AgInCl_6$ double perovskites is attributed to STEs [8, 12]. However, further investigation is required to comprehend the optical and charge carrier properties of this class of metal halide perovskites.

Conclusion

In summary, the evolution of advanced optoelectronic materials has shifted from quantum dots to diverse metal halide perovskite nanostructures. Metal halide perovskites, such as Bi-, Sn-, or In-based variants, hold potential for light harvesting and emission as alternatives to Pb-based materials. Sn-based 2D perovskites and In-based double perovskites exhibit efficient white light generation at room temperature using STEs, while Bi-based vacancy-ordered perovskites enable phonon-coupled slow cooling of hot carriers for energy conversion. Nevertheless, addressing challenges like poor carrier diffusion in vacancy-ordered perovskites, instability in Sn-based metal halides, and a less understood optoelectronic properties in metal ion-doped double perovskites is crucial to fully exploit these Pb-free alternatives in shaping the future technological landscape.

Acknowledgements

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Dr. Sushant Ghimire earned his PhD in 2020 in Environmental Material Science from Hokkaido University, Japan. Following this, he became an Alexander von Humboldt Fellow at the University of Rostock, Germany, collaborating with Prof. Christian Klinke on lead-free metal halide perovskite synthesis and spectroscopic studies. Joining Prof. Jochen Feldmann's group at Ludwig-Maximilians-Universität München in 2023, he now leads the *Photocatalysis and Novel Materials* team. Dr. Ghimire focuses on non-toxic semiconductor nanostructures, including quantum dots, for potential applications in light emission and photocatalysis, with a keen interest in understanding exciton/charge carrier dynamics using ultrafast spectroscopy such as transient absorption and time-resolved photoluminescence spectroscopy.