White Light Emission from 2D Layered Perovskites: Self-Trapped Exciton Mechanism

Katerina DeOlivares
BS/MS Chemistry/Materials Science
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Ongoing Challenges in LED Lighting Industry

Producing white light is particularly challenging

1. Efficiency
2. Color tone
3. Stability

Techniques for Producing White Light

Current LED sources of white light

1. Poor color quality
2. Lowered efficiency

Alternative intrinsic sources of white light

2D hybrid metal halide perovskites are a prime candidate

Figure 1a,b: “Solid-State Lighting: LED Basics” Office of Energy Efficiency & Renewable Energy
Figure 2: “New approach improving stability and optical properties of perovskite film” City University of Hong Kong (2019)
Structure of a 3D Perovskite

3D Perovskite vs. 2D Layered Perovskite


\[ \text{ABX}_3 \]

\[ (A')_m(A)_{n-1}B_nX_{3n+1} \]
Structure of 2D Hybrid Halide Perovskites

EDBE = \( \text{H}_2\text{N} - \text{O} - \text{O} - \text{NH}_2 \)

\[(\text{EDBE})\text{PbBr}_4\]

Synthetic Route to Layered Hybrid Perovskites

2D layered perovskites self-assemble

- **Hydrogen bonding** interactions

Spin coating self-assembly for thin films

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Figure 1: Liu Y et al. “Self-Assembly of Two-Dimensional Perovskite Nanosheet Building Blocks into Ordered Ruddlesden-Popper Perovskite Phase” J. Am. Chem. Soc. 141, 13028-13032 (2019)

Figure 2: Yan, Y et al. “Implementing an intermittent spin-coating strategy to enable bottom-up crystallization in layered halide perovskites”, nature communications, 12, 6603 (2021)
2D Hybrid Perovskites Produce Broadband Emission

Emission spectra of (EDBE)PbBr₄

Proposed Mechanism for Broad Emission:
Formation of self-trapped excitons

Distinguishing Between Excitons

**Exciton:** Bound state of an electron and hole that forms upon excitation

**Free Exciton:** Delocalized exciton that can move through the crystal
- Typically associated with narrow emission

**Trapped Exciton:** Exciton trapped in a low potential well by local lattice distortions
- Lattice distortion can be transient or permanent defect in lattice
- Often associated with broad emission

Excitons Can Cause Lattice Distortions

STEs behave like small **polarons**

Polarons: charge carriers that displace neighboring ions in the lattice

Excitons can also displace lattice:

- In 2D perovskite, organics create "softer lattice"
- More susceptible to distorting

Defect Trapping vs Intrinsic Self-Trapping

**Defect Trapping:** Exciton is trapped in a low potential state by a permanent defect in lattice

**Self-Trapping:** Exciton formation causes lattice distortion and then becomes trapped in a low potential state by the distorted lattice

Self-Trapped Excitons and Broad Emission

Self trapped exciton state is distorted from free exciton state

Distorted state results in range of emission wavelengths

Evidence for Self-Trapped Exciton Formation

- Decrease in temperature = more narrow emission
- Due to decrease in vibrations and less phonon coupling

Evidence is not complete...

Defects May be Responsible for Broad Emission

$\text{(PEA)}_2\text{PbI}_4$:  

Iodine vacancies cause broad emission

Evidence:

• Broad emission not observed for different synthetic routes

Defect induced in-gap trap states

White Light Emission is Highly Tunable in 2D Perovskites

Altering halogen component shifts wavelength of light on spectrum

- More electronegative halides = higher energy emission
- Chlorine compound is more blue-shifted

Efficiencies Need to be Improved

\[ \text{PLQY} = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} \]

Generation 1 2D Hybrid Halide: (N-MEDA)[PbBr\(_4\)]

Generation 2 2D Hybrid Halides: (EDBE)[PbBr\(_4\)]

PLQY = 1.5%

PLQY = 9%

Figure 1: Dohner, E et al. Self-Assembly of Broadband White-Light Emitters, J. Am. Chem. Soc. 136, 5, 1718-1721 (2014)

Figure 2: Dohner, E et. al. Intrinsic White-Light Emission from Layered Hybrid Perovskites, J. Am. Chem. Soc. 136, 38, 13154-13157 (2014)
Other Concerns with Hybrid Lead Halide Perovskites

Key Takeaways

• 2D hybrid structure promotes exciton-phonon coupling and self-trapped exciton formation

• Broad emission is generally attributed to self-trapped excitons

• Intermediate trap states or extrinsic defects could also cause broad emission in certain 2D materials

• 2D Layered perovskites require a higher efficiency and improved stability to be practical.
References

• Welles, H.L. Uber die Casium- und Kalium-Bleihalogenide, Sheffield Scientific School, New Haven, Conn (1893)
• Hou, L et al. Mn-doped 2D Sn-based perovskites with energy transfer from self-trapped excitons to dopants for warm white light-emitting diodes. J. Mater. Chem. C, 8, 8502-8506 (2020)
• Li, N et al. Shedding light on the energy applications of emerging 2D hybrid organic-inorganic halide perovskites. iScience, 25, 2 (2022)
• Kahmann, S et. al “Extrinsic nature of the broad photoluminescence in lead iodide-based Ruddlesden-Popper perovskites” Nature Communications, 11, 2344 (2020)
• Yin, J et. al “Modulation of Broadband Emissions in Two-Dimensional <100>-Oriented Ruddlesden-Popper Hybrid Perovskites”, ACS Energy Lett. 5, 7, 2149-2155 (2020)
Questions?