iScience

CellPress
OPEN ACCESS

Perspective

Dual-edged sword of ion migration in perovskite materials for simultaneous energy harvesting and storage application

Ramesh Kumar,[1,2,3] Monojit Bag,[3] and Sagar M. Jain[1,*]

SUMMARY

Portable electronic devices and Internet of Things (IoT) require an uninterrupted power supply for their optimum performance and are key ingredients of the futuristic smart buildings - cities. The off-grid photovoltaic cells and photo-rechargeable energy storage devices meet the requirements for continuous data processing and transmission. In addition, these off-grid devices can solve the energy mismanagement problem famously called as "duck curve". The conventional approach is the external integration of a photovoltaic cell and an energy storage device through a complex multi-layered structure. However, this approach causes ohmic transport losses and requires additional complex device packaging leading to increased weight and high cost. Toward this narrative, in this viewpoint, we shed light on application of disruptive organic-inorganic hybrid halide perovskite bifunctional materials employed as smart photo-rechargeable energy devices. We also present hybrid halide lead-free perovskite materials for off-grid energy storage systems for indoor lighting applications.

MAIN

Advanced integrated solar energy harvesting and storage technologies can play a key role in electrifying smart cities. It is essential to combine the energy harvest and storage technologies because irregularity in availability of solar energy on Earth. Moreover, solar power availability and hence generation is affected by the weather conditions, time of the day, cloud, shadow, rain, snow, and dust. The difference in available solar energy and energy demand throughout the day (energy mismanagement) is famously described by the so-called "Duck curve".[1] The duck curve is a graph of power production over the course of a day that shows the timing imbalance between peak demand and solar power generation. The name duck curve is derived from the shape of the curve. According to the duck curve, solar energy has highest yield during the day. While during night the solar energy production goes down. This requires conventional, on-grid energy to ramp-up quickly to meet electricity demands during the night. In a scenario, where solar energy is in excess to that of the required demand there requires a timely energy storage option. This energy management, balancing act between energy supply and demand is challenging and can waste a significant amount of solar energy unless stored properly. Given the recent breakthrough in harvesting solar energy specifically by disruptive 3rd generation photovoltaics, it becomes very timely to research new, smart ways to store electricity.

In this direction, off-grid energy resources have become an integral part of scientific research to meet the energy demand for portable smart electronics.[2–7] In recent years, off-grid energy storage devices have gained much more attention to fulfill cost-effective and environmentally friendly energy solutions in self-sustainable electronics, also in developing countries and in remote areas. The novel integrated devices can have the potential to efficiently harvest and store renewable solar energy and are referred as bifunctional devices. This technology by energy storage have potential to reduce and possibly eliminate the risk of wastage of excess solar energy generated during daytime and make it available during much required night time. In addition, these devices provide continuous data processing and transmission for the Internet of Things, smart cities, smart remote sensors, and autonomous integrated devices.[8–10]

The 3 approaches to integrate energy harvesting and storage devices are discussed in detail in the following text.

(1) Conventional approach - A well-known approach is integration of devices that include an external combination of a separate/independent energy harvesting (solar photovoltaic) part and a storage component (battery or supercapacitor) (Figure 1A). For instance, researchers demonstrated the integration of Si- and perovskite-based solar cells (PSC) with a solid-state lithium-ion battery (LIB), a flexible solid-state graphene-based supercapacitor, or a lithium-ion capacitor (Figure 1A).[11–19] However, this external integration

---

[1] Center for Renewable and Low Carbon Energy, School of Water, Energy and Environment (SWEE), Cranfield University, Cranfield MK430AL, UK
[2] Department of Chemistry, Ångström Laboratory, Uppsala University, Box 523, 75120 Uppsala, SE, Sweden
[3] Advanced Research in Electrochemical Impedance Spectroscopy (AREIS) Laboratory, Indian Institute of Technology Roorkee, Roorkee 247667, India
*Correspondence: sagar.m.jain@cranfield.ac.uk

https://doi.org/10.1016/j.isci.2023.108172

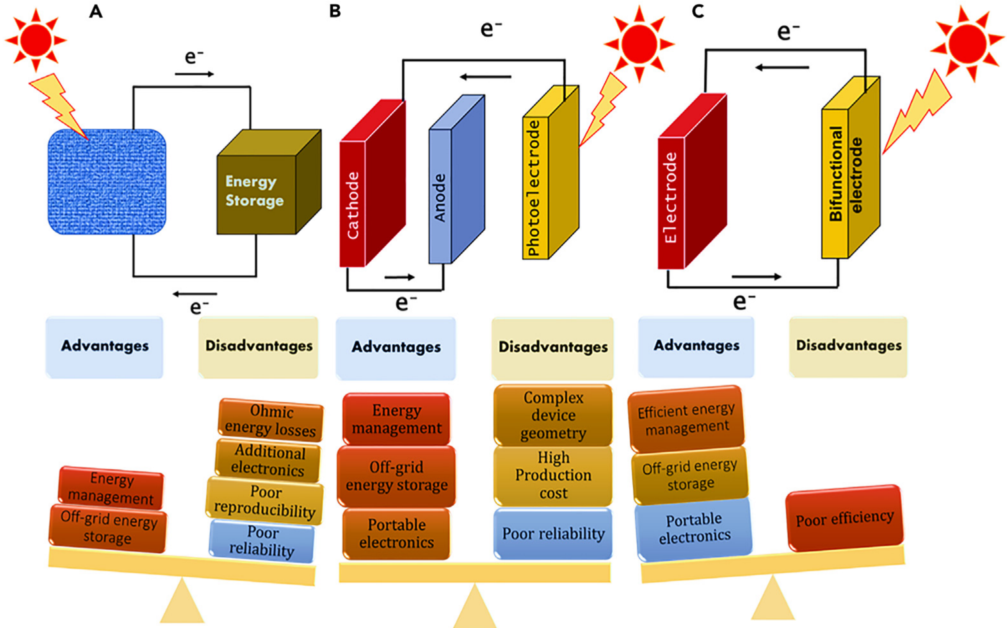

Figure 1. Integration of various types of solar energy conversion and storage systems for off-grid energy storage devices, and advantages and disadvantages of these integration systems

(A) Conventional integration of solar cells with energy storage equipment in series.

(B) Multilayer device with a photoelectrode.

(C) Innovative two-electrode device based advanced bifunctional materials.

introduces energy losses, poor reproducibility, and reliability as it requires additional electronics to match the output voltage with the energy storage system.

(2) Multilayer approach - An integrated device consists of a multilayer device structure where one of the electrodes could be common to surpass some issues of energy losses and reduce packaging volume to increase volumetric capacity (Figure 1B). In this direction, scientific community has started to integrate fibre-shaped super capacitors with a dye-sensitized solar cell or perovskite solar cell sharing an electrode. However, increasing complexity in the device structure increases the production cost.

(3) Advanced approach - Very recently, scientists and engineers have been trying to couple solar technology with energy storage technology by advanced photo electrodes, which have the bifunctional characteristics of energy harvesting and storage in the same material.[5] (Figure 1C). There have been some recent works towards graphitic carbon nitride, vanadium pentoxide/dioxide, and molybdenum disulphide–zinc oxide-based photo-electrodes for photo-rechargeable batteries and ion-capacitors that can directly harvest and store energy without the need for additional photovoltaic devices.[2–4,17–19] Therefore, these devices are the best alternative for self-charging or continuous power supply devices. However, these materials have poor cyclic stabilities, low energy storage capacities, and very low photo-charging conversion efficiency.

In our recent work, Jain et al.[20] employed inexpensive poly(3-hexylthiophene-2,5-diyl P3HT + Carbon paste as hole transport layer that showed 300 h of stability under continuous 1 sun illumination, without the use of an ultra violet-filter.

WHY HYBRID HALIDE PEROVSKITE FOR BIFUNCTIONAL DEVICES?

Hybrid halide perovskites (HHPs) are wonder materials as next-generation energy conversion and emerging as prominent energy storage option for portable electronic devices. HHP materials are a strong candidate for bifunctional operation of energy harvesting and storage applications due to their unique properties, such as ideal high absorption,[21,22] long carrier diffusion length (10–15 μm),[23,24] and mixed electronic-ionic conductivity.[25] The tuneable optical band gap of the HHPs may allow it to better align with the solar spectrum, which plays a vital role in the overall photo-charging conversion efficiency of the device. In the last ten years, organic-inorganic hybrid halide perovskite materials have been widely used in photovoltaic devices,[26,27] light-emitting diodes,[28,29] resistive switchings,[30,31] and sensor application[32,33] due to their extraordinary photophysical and suitable optoelectronic properties. Last but not least, the ease of manufacturing perovskite-based optoelectronics employing solution-based fabrication techniques provides a non-expensive route for its large-scale production.

The fundamental property of ion migration found in HHPs can act as double-edged sword (Figures 2A and 2B). Where ion migration can act notoriously and detrimental for the stability of electronic devices and various anomalous behavior within device. (Figure 2C). However, if

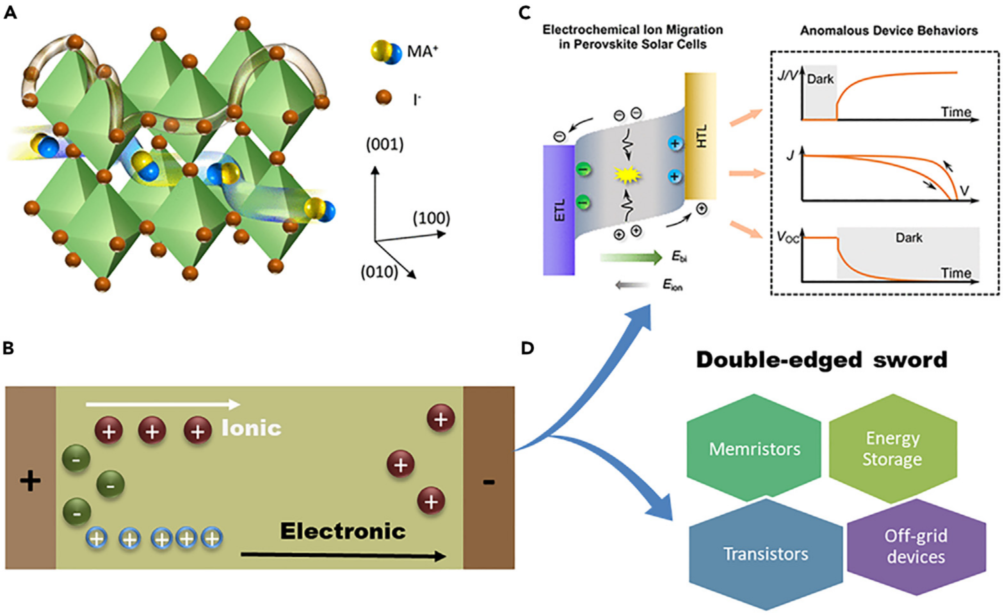

Figure 2. Ion dynamics in halide perovskites

(A) Ion migration through various channels in perovskite crystal structure. Reproduced with permission from the American Chemical Society 2016.[34]

(B) Mixed electronic-ionic conduction in halide perovskites. Reproduced with permission from the American Chemical Society 2021.[35]

(C) Various anomalous behavior in perovskite solar devices due to iontronics.

(D) Application of ion migration in various smart electronics.

employed in charge storage application, the same ion migration characteristics of HHPs pave a way for manufacturing advanced bifunctional devices, memristors, transistors and energy storage devices (Figure 2D).

Recently, HHPs are entering the energy storage application owing to their mixed electronic-ionic semiconductor and superior optical properties.[36] There have been some reports on perovskites-based lithium-ion batteries and supercapacitors. However, use of these materials in energy storage applications is limited due to poor stabilities and low energy capacities. But, these photo-active materials could be promising as advanced bifunctional electrodes for off-grid energy storage in smart sensors, IoT, and low-power portable electronic devices. Researchers have recently reported HHPs based Li-ion photo-rechargeable batteries.[37,38] Typical stumbling blocks of photo-rechargeable batteries are prolonged charging/discharging time and low power density.

To minimize and even to eliminate the drawback of low power density of photo-rechargeable batteries and photo-rechargeable electrochemical supercapacitors are alternative energy storage devices with the high-power density and moderate energy density as well as a fast-charging rate.[39] Photo-electrochemical cells typically consist of a thin electrolyte sandwich between two electrodes. The electrode materials are generally porous in order to increase the active surface area. One of the electrodes must be photo-activated for bifunctional applications in a single device. "One of the key criteria for the fabrication of an efficient photo-rechargeable supercapacitor is to design a photo-activated electrode and electrolyte material with high ionic, electronic conduction as well as high photo-response material." HHPs are known to have a higher absorption coefficient, photo-response, ionic conductivity as well as electronic conductivity.[40,41]

For this reason, HHPs are emerging as one of the promising technologies for photo-rechargeable energy storage applications for next-generation remote sensing devices. Recently, we reported efficient and stable halide-based perovskite electrochemical cells using non-aqueous electrolyte and single crystals powder.[39,42,43] Due to high absorption and mixed ionic-electronic semiconducting properties, these advanced photo-active materials can simultaneously harvest solar energy and store it in a single material. It is expected that the combination of halide perovskite and carbon quantum dots can have even very high capacities.[39,44] Moreover, the diffusion of organic/inorganic cation and halide anion plays a significant role in the charge storage in perovskite-based electrochemical cells. Therefore, various mixed cation and mixed halide perovskites combinations should be explored to achieve high photo-charging efficiency and photovoltage response. Hence, these multifunctional materials could be revolutionary to meet the sustainable energy crisis.

In photo-rechargeable capacitors, the device performance is primarily dependent on maintaining a balance between optical, electronic, and ionic conductivities when exposed to light. The appropriate balance between optical and electronic-ionic conductance is required in halide perovskites-based photo-rechargeable capacitors to achieve their dual-functionality of simultaneously store and harvest sun energy. Therefore, the coupling between electrons and ions in the perovskite active layer plays very crucial role of charge storage and generation capacities. Bag et al. and Jain et al.[40,41,45] respectively demonstrated that the ionic conductivity and optical properties of the perovskite materials can be tuned by changing the A-site cation and further tuned by substituting the X-site halide ion. Align to this in our recent work, we combined three features of hybrid perovskites: (a) absorption light in the solar spectrum, (b) efficient charge transport, and (c) photo-induced

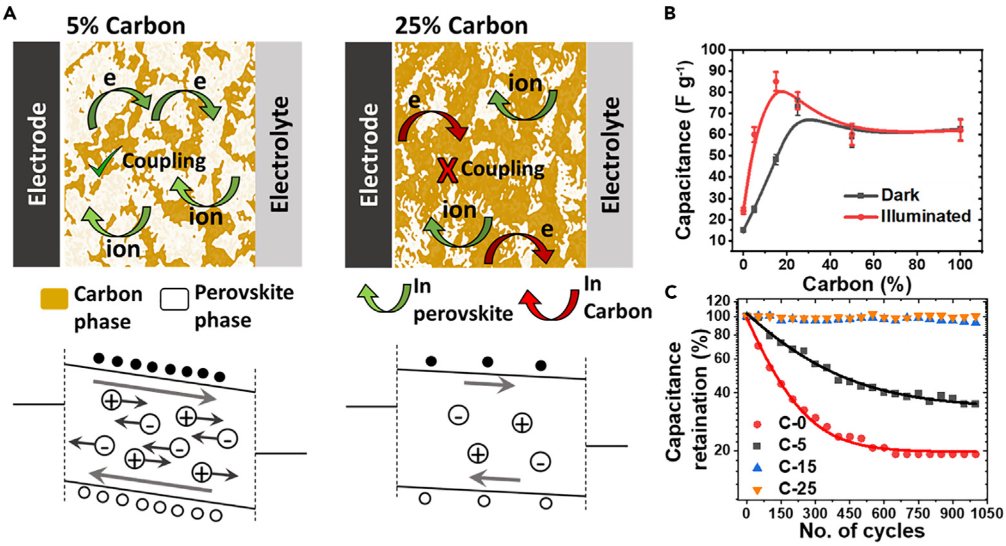

Figure 3. Device kinetics of perovskite-based photo-rechargeable ion capacitors

(A) Schematic illustrations of electronic-ionic charge transport in different perovskite-carbon phases and corresponding band bending diagrams. Reproduced with permission from the American Chemical Society 2022.[46]

(B and C) Variation of photo-capacitance and long-term cyclic stability with increase in carbon concentration. Figure reproduced with permission from the American Chemical Society 2022.[46]

ion migration to fabricate photo-rechargeable electrochemical cell with energy density of ∼30.71 Wh/kg and power density ∼1875 W/kg.[46] A key advance we reported in aforementioned work is the incorporation of carbon as efficient electronic agent into perovskite material to find the sweet spot between ionic, electronic, and optical properties. This will ultimately enable the fabrication of efficient photo-rechargeable electrochemical cell. Additionally, perovskite-carbon composite improves overall long-term stability. Here in Figure 3 (a) we ascribe two scenarios:

(1) Incorporation of minimal concentration of carbon (∼5%) in perovskite this causes the influx of electronic charge and ion migration transport predominantly via perovskite phase. Therefore, photo-generated charge transfers in the perovskite/electrode interface give rise to additional photo-capacitance (Figures 3A and 3B). However, improved photo-induced ion migration in the perovskite phase triggers the decomposition of the perovskite material resulting in a higher degradation rate, see Figure 3C.
(2) In later case, where incorporation of carbon is higher (∼25%) in perovskite this results into formation of carbon dominating phase which provides negligible photo response leading to low photo capacitance. However, as increased carbon phase restricts ion migration in perovskite phase causing improved stability.

Therefore, we expect that optimum ratio of electronic agents and perovskite materials will open a new avenue in the area of efficient as well stable photo-rechargeable energy storage applications.

Recently, Tanuj et al., demonstrated that the performance of photo-rechargeable supercapacitors, particularly in terms of photo-capacitance, is significantly impacted by the method used to synthesize the halide perovskites.[47] When different proportion of halide perovskite in powder form is physically combined, they tend to exhibit nanoscale phase separation in the resulting blend of perovskite material. This phase separation results in the interconnected domains rich in bromide and iodide components. Notably, holes originating from the bromide-rich domains can undergo thermal migration to the iodide-rich domains, where they recombine with electrons.

LIMITATIONS OF THE STUDY

The ion migration is one of the key reasons for the operational instability of perovskite material.[48] In addition, lead (Pb) in conventional perovskites hinders their commercial use due to issues like lead leakage, sensitivity to moisture and temperature. This raises concerns about environmental and health impacts. To address this, research focuses on encapsulation and coating methods for future perovskite technology.

To tackle the stability challenges, various strategies are explored. Some key experimental strategies are ascribed in the following text.

(1) Incorporating polymers into perovskite matrices: One approach involves integrating polymers into the perovskite material itself. This method can enhance perovskite structure stability and make a right balance between optical and electro-ionic properties.[49,50] Polymers serve as a supportive matrix, reinforcing the structural integrity and long-term performance of photo-rechargeable supercapacitors.

(2) Dimensional engineering: Another method is to employ dimensional engineering techniques. This entails tailoring the dimensions and architecture of the materials used in supercapacitor construction. By precisely designing the physical properties of components, researchers can optimize performance while reducing the risk of stability issues linked to huge ion migration. Very recently, we have a proposed 2D/3D perovskite hetero-structure to improve the performance and stability of photo-ion capacitors for IoTs and smart sensors.[51]
(3) Adopting gel electrolytes instead of liquid: Replacing conventional liquid electrolytes with gel-based alternatives for improving the stability of perovskite material. Gel electrolytes offer several advantages, including decreased ion mobility and improved stability. They effectively immobilize ions, minimizing the likelihood of migration-related performance degradation. This approach enhances the overall longevity and dependability of photo-rechargeable supercapacitors."
(4) Perovskite-carbon composite: Employing carbon composite materials such as graphene, C60, and P3HT in perovskite solar cells[52] has shown great potential owing to their low-cost production and superior stability in air, compared to their counterparts using metal contacts. However, one of the major obstacles for maintaining the higher performance of these carbon composite solar cells is that the hole transport materials developed for state-of-the-art Au-based PSCs are not suitable for carbon-based PSCs.

In our recent work, Jain et al.[20] employed inexpensive poly(3-hexylthiophene-2,5-diyl P3HT + Carbon paste as hole transport layer that showed 300 h of stability under continuous 1 sun illumination, without the use of an ultra violet-filter.

LEAD-FREE PEROVSKITES FOR SMART INDOOR APPLICATIONS/INDOOR LIGHT RECYCLING

Indoor photovoltaics (PV) devices have received excellent research attention from the PV scientific community due to plethora of applications in the Internet of Things (IoT) for smart cities.[8,53] There are various existing PV technologies for indoor light recycling for smart electronic devices, such as silicon, cadmium telluride (CdTe), and copper indium gallium selenide (CIGS), and polymer-based photovoltaic devices. The perovskite-based solar cells (PSCs) are promising for indoor light harvesting due to their low cost of manufacturing, visible color-tunability, lightweight, and flexibility. Lead-based PSCs already reached over 25% efficiency under 1 sun illumination (condition of a typical sunny day).[27] However, device instability in the ambient environment is a serious concern for outdoor application of PSCs. The power conversion efficiency of PSCs increases under low-intensity, artificial indoor light due to better spectral matching between their absorption and the irradiance spectrum. In this direction, our previous work experimentally demonstrated >35% efficiency under indoor illumination (1000 lux).[54,55] Also, these devices are more stable under artificial light due to less ion migration.[21] Nevertheless, efficient energy harvesting and storage is still a concern with harvesting under indoor lighting applications.

Bifunctional energy storage and harvesting devices could be a promising technology for next-generation energy management resources and applications in the field of the Internet of Things (IoT) for smart cities. The high performance of PSCs under white LED lights coupled with their energy storage properties due to high ionic and electronic conductivities, solution-processable, flexible, low-weight, semitransparent, and tunable bandgap properties that will open a wider variety of indoor light recycling applications for smart cities.

REQUIREMENT FOR LEAD-FREE PEROVSKITE FOR INDOOR LIGHT HARVESTING

Lead-based perovskite has already proven more efficient than traditional silicon photovoltaics. However, there are two major bottlenecks for its commercialization: (1) Long-term stability and (2) Toxicity of material, in particular lead metal used in these solar cells. While, there are many breakthroughs in improvement for stability of lead-based perovskite solar cells,[56–59] there still exists a major disadvantage for presence of lead in these solar cells.

WHY LEAD IS TOXIC?

When it comes to toxicity of lead-based perovskite solar cells, we often hear a counter argument mentioning the batteries (lead-acid batteries) do contain lead but are very commonly used till date. Despite, there are clear evidence that this has catastrophic effect if such lead-acid batteries are not handled with safety and care.[60] Perovskite solar cells contain lead in its 2^+ oxidation state as Pb^{2+} that is coordinated to $2I^-$ ions. Now when this Pb^{2+} comes in close vicinity with water or even humidity from ambient air it can get dissolved and leach out of the PbI_6 octahedron structure dissolving in water. It is shown previously that Pb^{2+} is more miscible in cold water as the process is exothermic. The impact of toxicity of lead on living beings and environment is well documented recently in many articles.[61–63] The concern of lead toxicity is more serious when one wishes to use lead-based perovskite solar cells for indoor light harvesting. Hence, this is crucial to explore lead-free perovskite materials for bifunctional electrodes that simultaneously can harvest and store indoor light for futuristic applications.

CONCLUSIONS

Off-grid energy systems are in high demand because of their application in the Internet of Things (IoT), smart cities, intelligent remote sensors, and autonomous integrated devices. In this viewpoint, we have discussed different types of integration of solar energy conversion and storage systems for off-grid energy storage devices, and advantages and disadvantages of these integration systems. Moreover, we shed light on organic-inorganic hybrid halide perovskite (OIHHP) multifunctional materials for photo-rechargeable energy storage devices for next-generation smart portable electronic appliance. An overview of the current state of bifunctional energy storage devices and discuss the challenges in this technology, moreover, we also present hybrid halide lead-free perovskite materials for off-grid energy storage systems for indoor light management.

Few challenges such as how to manage both energy storage and harvesting employing single material for engineering of bifunctional device? What optoelectronic properties, characteristics are key in defining bifunctionality (energy harvesting and storage capabilities)? remain unanswered till date.

ACKNOWLEDGMENTS

Ramesh Kumar is a Commonwealth Scholar, funded by the UK Government and Ministry of Education, Government of India for PhD fellowship. M.B. acknowledges Science and Engineering Research Board (SERB), INDIA under award no. CRG/2021/001744 dated 07/03/2022 for partial support to carry out this research work. R.K. also acknowledges Ministry of Education, Government of India for PhD fellowship. Sagar M Jain acknowledges Commonwealth fellowship for funding support for this work.

AUTHOR CONTRIBUTIONS

Conceptualization, R.K., M.B., and S.M.J.; Investigation, R.K., M.B., and S.M.J.; Interpretation, R.K., M.B., and S.M.J.; Compilation, R.K., M.B., and S.M.J.; Visualization, R.K.; Supervision, M.B. and S.M.J.; Funding acquisition, M.B. and S.M.J.; Writing – Original draft, R.K.; Writing.–.Review and editing, R.K., M.B., and S.M.J.

DECLARATION OF INTERESTS

The authors declare no competing financial interests.

INCLUSION AND DIVERSITY

We support inclusive, diverse, and equitable conduct of research.

REFERENCES

1. Confronting the duck curve: how to address over-generation of solar energy | Department of energy. https://www.energy.gov/eere/articles/confronting-duck-curve-how-address-over-generation-solar-energy.
2. Deka Boruah, B., and De Volder, M. (2021). Vanadium dioxide-zinc oxide stacked photocathodes for photo-rechargeable zinc-ion batteries. J. Mater. Chem. A Mater. *9*, 23199–23205. https://doi.org/10.1039/d1ta07572a.
3. Boruah, B.D., Wen, B., Nagane, S., Zhang, X., Stranks, S.D., Boies, A., and De Volder, M. (2020). Photo-rechargeable Zinc-Ion Capacitors using V2O5-Activated Carbon Electrodes. ACS Energy Lett. *5*, 3132–3139. https://doi.org/10.1021/acsenergylett.0c01528.
4. Boruah, B.D., Mathieson, A., Wen, B., Jo, C., Deschler, F., and De Volder, M. (2020). Photo-Rechargeable Zinc-Ion Capacitor Using 2D Graphitic Carbon Nitride. Nano Lett. *20*, 5967–5974. https://doi.org/10.1021/acs.nanolett.0c01958.
5. Lv, J., Xie, J., Mohamed, A.G.A., Zhang, X., and Wang, Y. (2022). Photoelectrochemical energy storage materials: design principles and functional devices towards direct solar to electrochemical energy storage. Chem. Soc. Rev. *51*, 1511–1528. https://doi.org/10.1039/d1cs00859e.
6. Namsheer, K., and Rout, C.S. (2021). Photo-powered integrated supercapacitors: a review on recent developments, challenges, and future perspectives. J. Mater. Chem. A Mater. *9*, 8248–8278. https://doi.org/10.1039/d1ta00444a.
7. Li, C., Cong, S., Tian, Z., Song, Y., Yu, L., Lu, C., Shao, Y., Li, J., Zou, G., Rümmeli, M.H., et al. (2019). Flexible perovskite solar cell-driven photo-rechargeable lithium-ion capacitor for self-powered wearable strain sensors. Nano Energy *60*, 247–256. https://doi.org/10.1016/j.nanoen.2019.03.061.
8. Mainville, M., and Leclerc, M. (2020). Recent Progress on Indoor Organic Photovoltaics: From Molecular Design to Production Scale. ACS Energy Lett. *5*, 1186–1197. https://doi.org/10.1021/acsenergylett.0c00177.
9. Raj, A., and Steingart, D. (2018). Review—Power Sources for the Internet of Things. J. Electrochem. Soc. *165*, B3130–B3136. https://doi.org/10.1149/2.0181808jes.
10. Biswas, S., and Kim, H. (2020). Solar cells for indoor applications: Progress and development. Polymers *12*, 1338. https://doi.org/10.3390/POLYM12061338.
11. Chen, P., Li, T.T., Yang, Y.B., Li, G.R., and Gao, X.P. (2022). Coupling aqueous zinc batteries and perovskite solar cells for simultaneous energy harvest, conversion and storage. Nat. Commun. *13*, 64–69. https://doi.org/10.1038/s41467-021-27791-7.
12. Liang, J.J., Chou, M.W., Lin, Y.L., Zhao, P., Wang, Y., Hu, Y., Ma, L., Tie, Z., Liu, J., and Jin, Z. (2018). An all-inorganic perovskite solar capacitor for efficient and stable spontaneous photocharging. Nano Energy *8*, 239–245. https://doi.org/10.1016/j.nanoen.2018.07.060.
13. Wang, L., Wen, L., Tong, Y., Wang, S., Hou, X., An, X., Dou, S.X., and Liang, J. (2021). Photo-rechargeable batteries and supercapacitors: Critical roles of carbon-based functional materials. Carbon Energy *3*, 225–252. https://doi.org/10.1002/cey2.105.
14. Liu, Z., Zhong, Y., Sun, B., Liu, X., Han, J., Shi, T., Tang, Z., and Liao, G. (2017). Novel Integration of Perovskite Solar Cell and Supercapacitor Based on Carbon Electrode for Hybridizing Energy Conversion and Storage. ACS Appl. Mater. Interfaces *9*, 22361–22368. https://doi.org/10.1021/acsami.7b01471.
15. Zhang, X., Song, W.L., Tu, J., Wang, J., Wang, M., and Jiao, S. (2021). A Review of Integrated Systems Based on Perovskite Solar Cells and Energy Storage Units: Fundamental, Progresses, Challenges, and Perspectives. Adv. Sci. *8*, 2100552. https://doi.org/10.1002/ADVS.202100552.
16. Liang, J., Zhu, G., Lu, Z., Zhao, P., Wang, C., Ma, Y., Xu, Z., Wang, Y., Hu, Y., Ma, L., et al. (2018). Integrated perovskite solar capacitors with high energy conversion efficiency and fast photo-charging rate. J. Mater. Chem. A Mater. *6*, 2047–2052. https://doi.org/10.1039/c7ta09099d.
17. Boruah, B.D., Wen, B., and De Volder, M. (2021). Light Rechargeable Lithium-Ion Batteries Using V2O5Cathodes. Nano Lett. *21*, 3527–3532. https://doi.org/10.1021/acs.nanolett.1c00298.
18. Boruah, B.D., Wen, B., and De Volder, M. (2021). Molybdenum Disulfide-Zinc Oxide Photocathodes for Photo-Rechargeable Zinc-Ion Batteries. ACS Nano *15*, 16616–16624. https://doi.org/10.1021/acsnano.1c06372.
19. Boruah, B.D., Mathieson, A., Wen, B., Feldmann, S., Dose, W.M., and De Volder, M. (2020). Photo-rechargeable zinc-ion batteries. Energy Environ. Sci. *13*, 2414–2421. https://doi.org/10.1039/D0EE01392G.
20. Jain, S.M., Edvinsson, T., and Durrant, J.R. (2019). Green fabrication of stable lead-free bismuth based perovskite solar cells using a non-toxic solvent. Commun. Chem. *2*, 91. https://doi.org/10.1038/s42004-019-0195-3.
21. Bag, M., Renna, L.A., Adhikari, R.Y., Karak, S., Liu, F., Lahti, P.M., Russell, T.P., Tuominen, M.T., and Venkataraman, D. (2015). Kinetics of Ion Transport in Perovskite Active Layers and Its Implications for Active Layer Stability. J. Am. Chem. Soc. *137*, 13130–13137. https://doi.org/10.1021/jacs.5b08535.

22. Noh, J.H., Im, S.H., Heo, J.H., Mandal, T.N., and Seok, S.I. (2013). Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. Nano Lett. *13*, 1764–1769. https://doi.org/10.1021/nl400349b.
23. Rehman, W., McMeekin, D.P., Patel, J.B., Milot, R.L., Johnston, M.B., Snaith, H.J., and Herz, L.M. (2017). Photovoltaic mixed-cation lead mixed-halide perovskites: Links between crystallinity, photo-stability and electronic properties. Energy Environ. Sci. *10*, 361–369. https://doi.org/10.1039/c6ee03014a.
24. Zhang, W., Eperon, G.E., and Snaith, H.J. (2016). Metal halide perovskites for energy applications. Nat. Energy *1*, 16048. https://doi.org/10.1038/nenergy.2016.48.
25. Moia, D., and Maier, J. (2021). Ion Transport, Defect Chemistry, and the Device Physics of Hybrid Perovskite Solar Cells. ACS Energy Lett. *6*, 1566–1576. https://doi.org/10.1021/acsenergylett.1c00227.
26. Nie, W., Tsai, H., Asadpour, R., Blancon, J.-C., Neukirch, A.J., Gupta, G., Crochet, J.J., Chhowalla, M., Tretiak, S., Alam, M.A., et al. (2015). High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. Science *347*, 522–525.
27. Best research-cell efficiency chart | Photovoltaic research | NREL. https://www.nrel.gov/pv/cell-efficiency.html.
28. Tan, Z.K., Moghaddam, R.S., Lai, M.L., Docampo, P., Higler, R., Deschler, F., Price, M., Sadhanala, A., Pazos, L.M., Credgington, D., et al. (2014). Bright light-emitting diodes based on organometal halide perovskite. Nat. Nanotechnol. *9*, 687–692. https://doi.org/10.1038/nnano.2014.149.
29. Wang, N., Allali, G., Kesavadas, C., Noone, M.L., Pradeep, V.G., Blumen, H.M., Verghese, J., Sun, Y., Cao, Y., Yang, R., et al. (2016). Perovskite light-emitting diodes based on solution-processed self-organized multiple quantum wells. Nat. Photonics *50*, 699–707. https://doi.org/10.1038/nphoton.2016.185.
30. Hwang, B., and Lee, J.S. (2018). Lead-free, air-stable hybrid organic-inorganic perovskite resistive switching memory with ultrafast switching and multilevel data storage. Nanoscale *10*, 8578–8584. https://doi.org/10.1039/c8nr00863a.
31. Ercan, E., Chen, J.Y., Tsai, P.C., Lam, J.Y., Huang, S.C.W., Chueh, C.C., and Chen, W.C. (2017). A Redox-Based Resistive Switching Memory Device Consisting of Organic–Inorganic Hybrid Perovskite/Polymer Composite Thin Film. Adv. Electron. Mater. *3*, 1–8. https://doi.org/10.1002/aelm.201700344.
32. Gu, L., Poddar, S., Lin, Y., Long, Z., Zhang, D., Zhang, Q., Shu, L., Qiu, X., Kam, M., Javey, A., and Fan, Z. (2020). A biomimetic eye with a hemispherical perovskite nanowire array retina. Nature *581*, 278–282. https://doi.org/10.1038/s41586-020-2285-x.
33. Yu, X., Tsao, H.N., Zhang, Z., and Gao, P. (2020). Miscellaneous and Perspicacious: Hybrid Halide Perovskite Materials Based Photodetectors and Sensors. Adv. Opt. Mater. *8*, 2001095. https://doi.org/10.1002/ADOM.202001095.
34. Yuan, Y., and Huang, J. (2016). Ion Migration in Organometal Trihalide Perovskite and Its Impact on Photovoltaic Efficiency and Stability. Acc. Chem. Res. *49*, 286–293. https://doi.org/10.1021/acs.accounts.5b00420.
35. Liu, J., Hu, M., Dai, Z., Que, W., Padture, N.P., and Zhou, Y. (2021). Correlations between Electrochemical Ion Migration and Anomalous Device Behaviors in Perovskite Solar Cells. ACS Energy Lett. *6*, 1003–1014. https://doi.org/10.1021/acsenergylett.0c02662.
36. Zhang, L., Miao, J., Li, J., and Li, Q. (2020). Halide Perovskite Materials for Energy Storage Applications. Adv. Funct. Mater. *30*, 2003653. https://doi.org/10.1002/adfm.202003653.
37. Ahmad, S., George, C., Beesley, D.J., Baumberg, J.J., and De Volder, M. (2018). Photo-Rechargeable Organo-Halide Perovskite Batteries. Nano Lett. *18*, 1856–1862. https://doi.org/10.1021/acs.nanolett.7b05153.
38. Tewari, N., Shivarudraiah, S.B., and Halpert, J.E. (2021). Photorechargeable Lead-Free Perovskite Lithium-Ion Batteries Using Hexagonal Cs3Bi2I9Nanosheets. Nano Lett. *21*, 5578–5585. https://doi.org/10.1021/acs.nanolett.1c01000.
39. Kumar, R., and Bag, M. (2021). Hybrid Halide Perovskite Based Electrochemical Supercapacitors: Recent Progress and Perspective (Energy Technology), 2100889. https://doi.org/10.1002/ente.202100889.
40. Srivastava, P., Kumar, R., and Bag, M. (2021). Discerning the Role of an A-Site Cation and X-Site Anion for Ion Conductivity Tuning in Hybrid Perovskites by Photoelectrochemical Impedance Spectroscopy. J. Phys. Chem. C *125*, 211–222. https://doi.org/10.1021/acs.jpcc.0c09443.
41. Kumar, R., Srivastava, P., Bag, M., Kumar, R., and Srivastava, P. (2020). Role of A-Site Cation and X-Site Halide Interactions in Mixed-Cation Mixed-Halide Perovskites for Determining Anomalously High Ideality Factor and the Super-linear Power Law in AC Ionic Conductivity at Operating Temperature. ACS Appl. Electron. Mater. *2*, 4087–4098. https://doi.org/10.1021/acsaelm.0c00874.
42. Kumar, R., and Bag, M. (2021). Quantifying Capacitive and Diffusion-Controlled Charge Storage from 3D Bulk to 2D Layered Halide Perovskite-Based Porous Electrodes for Efficient Supercapacitor Applications. J. Phys. Chem. C *125*, 16946–16954. https://doi.org/10.1021/acs.jpcc.1c05493.
43. Kumar, R., Shukla, P.S., Varma, G.D., and Bag, M. (2021). Synthesis of porous electrode from CH3NH3PbBr3 single crystal for efficient supercapacitor application: Role of morphology on the charge storage and stability. Electrochim. Acta *398*, 139344. https://doi.org/10.1016/j.electacta.2021.139344.
44. Kumar, R., Kumar, J., Kadian, S., Srivastava, P., Manik, G., and Bag, M. (2021). Tunable ionic conductivity and photoluminescence in quasi-2D CH 3 NH 3 PbBr 3 thin films incorporating sulphur doped graphene quantum dots. Phys. Chem. Chem. Phys. *23*, 22733–22742. https://doi.org/10.1039/d1cp03621a.
45. Park, B.W., Philippe, B., Jain, S.M., Zhang, X., Edvinsson, T., Rensmo, H., Zietz, B., and Boschloo, G. (2015). Chemical engineering of methylammonium lead iodide/bromide perovskites: tuning of opto-electronic properties and photovoltaic performance. J. Mater. Chem. A Mater. *3*, 21760–21771. https://doi.org/10.1039/C5TA05470B.
46. Kumar, R., Kumar, A., Shukla, P.S., Varma, G.D., Venkataraman, D., and Bag, M. (2022). Photorechargeable Hybrid Halide Perovskite Supercapacitors. ACS Appl. Mater. Interfaces *14*, 35592–35599. https://doi.org/10.1021/ACSAMI.2C07440.
47. Kumar, T., Kumar, A., Beniwal, S., Kumar, R., and Bag, M. (2023). Photo-generated charge trapping in phase segregated halide perovskites-A comprehensive approach towards efficient photo-rechargeable ion capacitors. Batter. Supercaps *6*, e202300213. https://doi.org/10.1002/batt.202300213.
48. Sakhatskyi, K., John, R.A., Guerrero, A., Tsarev, S., Sabisch, S., Das, T., Matt, G.J., Yakunin, S., Cherniukh, I., Kotyrba, M., et al. (2022). Assessing the Drawbacks and Benefits of Ion Migration in Lead Halide Perovskites. ACS Energy Lett. *7*, 3401–3414.
49. Kumar, R., Kumar, A., Shukla, P.S., Varma, G.D., Venkataraman, D., and Bag, M. (2022). Photorechargeable Hybrid Halide Perovskite Supercapacitors. ACS Appl. Mater. Interfaces *14*, 35592–35599. https://doi.org/10.1021/acsami.2c07440.
50. Kumar, R., and Bag, M. (2022). Hybrid Halide Perovskite-Based Electrochemical Supercapacitors: Recent Progress and Perspective. Energy Tech. *10*, 2100889. https://doi.org/10.1002/ente.202100889.
51. Kumar, T., Thakuria, R., Kumar, M., Kumar, A., Kumar, R., and Bag, M. (2017). Sustainable Energy & Fuels Sustainable Energy & Fuels Accepted Manuscript Dimensional Engineering to Simultaneously Enhance Energy Density and Stability of MAPbBr3-Based Photo-Rechargeable Ion Capacitor †. https://doi.org/10.1039/D3SE00661A.
52. Litvin, A.P., Zhang, X., Berwick, K., Fedorov, A.V., Zheng, W., and Baranov, A.V. (2020). Carbon-based interlayers in perovskite solar cells. Renew. Sustain. Energy Rev. *124*, 109774. ISSN 1364-0321.
53. Cutting, C.L., Bag, M., and Venkataraman, D. (2016). Indoor light recycling: a new home for organic photovoltaics. J. Mater. Chem. C *4*, 10367–10370. https://doi.org/10.1039/C6TC03344J.
54. Li, M., Zhao, C., Wang, Z.K., Zhang, C.C., Lee, H.K.H., Pockett, A., Barbé, J., Tsoi, W.C., Yang, Y.G., Carnie, M.J., et al. (2018). Interface Modification by Ionic Liquid: A Promising Candidate for Indoor Light Harvesting and Stability Improvement of Planar Perovskite Solar Cells. Adv. Energy Mater. *8*, 1801509. https://doi.org/10.1002/AENM.201801509.
55. Pham, H.D., Jain, S.M., Li, M., Wang, Z.K., Manzhos, S., Feron, K., Pitchaimuthu, S., Liu, Z., Motta, N., Durrant, J.R., and Sonar, P. (2020). All-Rounder Low-Cost Dopant-Free D-A-D Hole-Transporting Materials for Efficient Indoor and Outdoor Performance of Perovskite Solar Cells. Adv. Electron. Mater. *6*, 1900884. https://doi.org/10.1002/AELM.201900884.
56. Kobayashi, E., Tsuji, R., Martineau, D., Hinsch, A., and Ito, S. (2021). Light-induced performance increase of carbon-based perovskite solar module for 20-year stability. Cell Rep. Phys. Sci. *2*, 100648. https://doi.org/10.1016/j.xcrp.2021.100648.
57. Wang, R., Mujahid, M., Duan, Y., Wang, Z.K., Xue, J., and Yang, Y. (2019). A Review of Perovskites Solar Cell Stability. Adv. Funct. Mater. *29*, 1808843. https://doi.org/10.1002/ADFM.201808843.
58. Kim, H.S., Seo, J.Y., and Park, N.G. (2016). Material and Device Stability in Perovskite

Solar Cells. ChemSusChem *9*, 2528–2540. https://doi.org/10.1002/cssc.201600915.

59. Fu, Q., Tang, X., Huang, B., Hu, T., Tan, L., Chen, L., Chen, Y., Fu, Q., Tang, X., Huang, B., et al. (2018). Recent Progress on the Long-Term Stability of Perovskite Solar Cells. Adv. Sci. *5*, 1700387. https://doi.org/10.1002/ADVS.201700387.
60. Africa's growing lead battery industry is causing extensive contamination. https://theconversation.com/africas-growing-lead-battery-industry-is-causing-extensive-contamination-130899.
61. Li, J., Cao, H.L., Jiao, W.B., Wang, Q., Wei, M., Cantone, I., Lü, J., and Abate, A. (2020). Biological impact of lead from halide perovskites reveals the risk of introducing a safe threshold. Nat. Commun. *11*, 310. https://doi.org/10.1038/s41467-019-13910-y.
62. Ponti, C., Nasti, G., Di Girolamo, D., Cantone, I., Alharthi, F.A., and Abate, A. (2022). Environmental lead exposure from halide perovskites in solar cells. Trends Ecol. Evol. *37*, 281–283. https://doi.org/10.1016/J.TREE.2022.01.002.
63. O'Connor, D., and Hou, D. (2021). Manage the environmental risks of perovskites. One Earth *4*, 1534–1537. https://doi.org/10.1016/J.ONEEAR.2021.11.002.