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HALIDE PEROVSKITES FOR PHOTONIC APPLICATIONS

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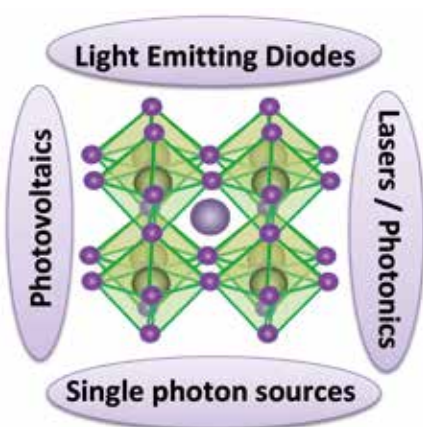
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Halide perovskites are a new class of semiconductors showing an incredible set of physical properties well-suited for a large range of opto-electronic applications. These physical properties can be easily tuned and adapted to the intended application by modifying the composition and the size of the material. Additionally, these materials are solution-processed at low temperature and ambient pressure, and contain earth-abundant elements. However, some important challenges remain: the presence of lead and the stability. In this paper, we present some outlines of

these materials in several fields of opto-electronics, *i.e.* photovoltaics and light-emitting devices, such as LEDs, single-photon sources, lasers, and photonics.

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A BX₃ perovskites constitute the oldest families of crystals described by crystallography: the calcium titanate CaTiO₃ was named a “perovskite” by the German mineralogist Gustav Rose around 1839 in honor of the Russian mineralogist Lev Alexeïevich Perovski. Since then, all compounds with ABX₃ stoichiometry are

called perovskites. Since 2009, the family of the halide perovskites is at the origin of a dazzling success in the field of photovoltaics shortly followed by outstanding results in the field of optoelectronic technologies: for this family, A is an organic (inorganic) monovalent cation such as methylammonium, formamidinium, (Cesium), B is a divalent metal usually lead, and X is a halogen such as I, Br or Cl (figure 1).

A phenomenal enthusiasm of the international community has followed the first encouraging results [1] to optimize the material itself and the perovskite-based devices and to understand the physical properties of this new class of semiconductors. Very rapidly, it appeared that halide perovskites have an impressive number of advantages which explain their success story [2]: an appropriate and adjustable bandgap which

can be easily tuned from the IR to the blue region of the electromagnetic spectrum by changing the halogen and allowing optimization of photon collection combined with a high absorption coefficient due to the direct nature of the bandgap (in the range of 10^4 to 10^5 cm^{-1}); large diffusion lengths (comparable to the ones in silicon) due to a long lifetime of the charge carriers; a surprising “defect tolerance”, *i.e.* the electronically benign nature of the most common point defects (vacancies and interstitials) with only shallow trap states close to the valence and conduction bands, favoring detrapping of carriers at room temperature and, hence, small non-radiative recombination rates; and finally, a large tunability of the exciton binding energy allowing to choose the optimal composition depending on the targeted application.

A remarkable advantage of the halide perovskites is the fact that they are synthesized in solution, under ambient to mildly elevated temperature and atmospheric pressure conditions, compatible with large surface deposition techniques and leading to lower production costs compared to silicon and other inorganic semiconductors. In addition to all these advantages, this family of compounds

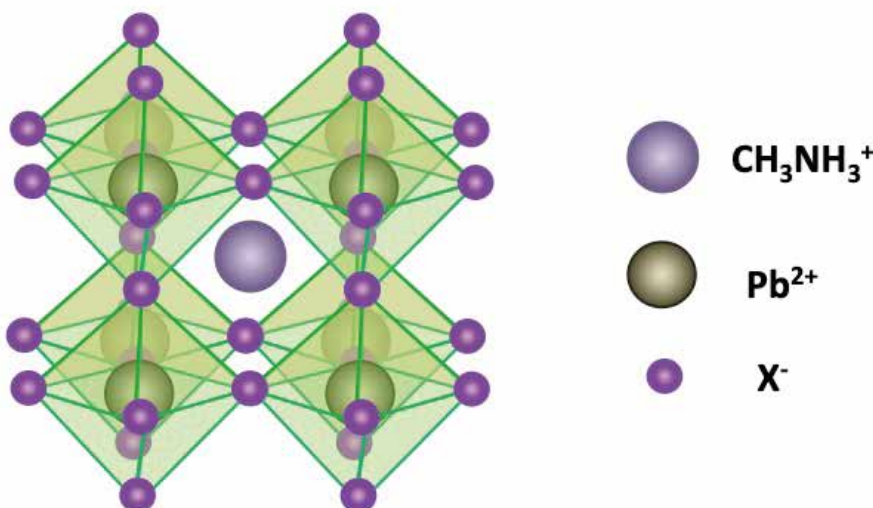
presents an exceptional chemical versatility, that is to say that it is possible to tune the physical properties by changing the material composition: as already mentioned changing the halogen ion or the divalent metal allows to tune the bandgap and, as another example, changing the organic cation or the synthesis procedure allows to tune the dimensionality of the density of states (3D: bulk, 2D: quantum wells, 1D: quantum wires, 0D: quantum dots) and then the excitonic and transport properties.

Thanks to this flexibility, the halide perovskites are not only efficient for photovoltaic applications, but also for other photonic ones. After presenting some outlines in the photovoltaic field, we will develop their various applications in the field of light emitting devices: LEDs, single photon sources, lasers, and photonics.

PHOTOVOLTAICS

The interest of the scientific community in halide perovskites for optoelectronics was triggered by the surprising performances achieved in 2012 by solid-state solar cells employing this material as a solar light absorber. After more than a decade of continuous improvement, the ●●●

Figure 1. Schematic crystal structure of $\text{CH}_3\text{NH}_3\text{PbX}_3$. Ionic bonds exist between the lead atoms and the X^- ions, thus forming inorganic PbX_6^{4-} octahedra, characteristic of the perovskite structure. These octahedrons touch each other at their vertex to form a 3D network. The CH_3NH_3^+ cation is placed on the interstitial sites between the octahedra.



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record power conversion efficiency (PCE) of a perovskite solar cell (PSC) is now achieving 25.7%. It is close to the record PCE of the mature crystalline silicon technology which appeared in the 1950's. The use of halide perovskite materials with small exciton binding energy facilitates the separation of electrons and holes after the absorption of solar photons. PSC requires asymmetric selective contacts for the collection of the charge carriers photogenerated in the absorber layer: the holes are collected by a specific p-type layer (HTL) which transports holes and blocks electrons while, at the opposite end of the cell, the electrons are transported by a specific n-type layer (ETL) which also blocks holes (fig 2). Various architectures have been developed depending

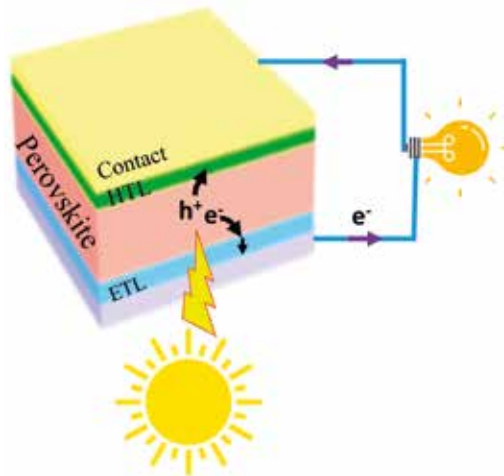
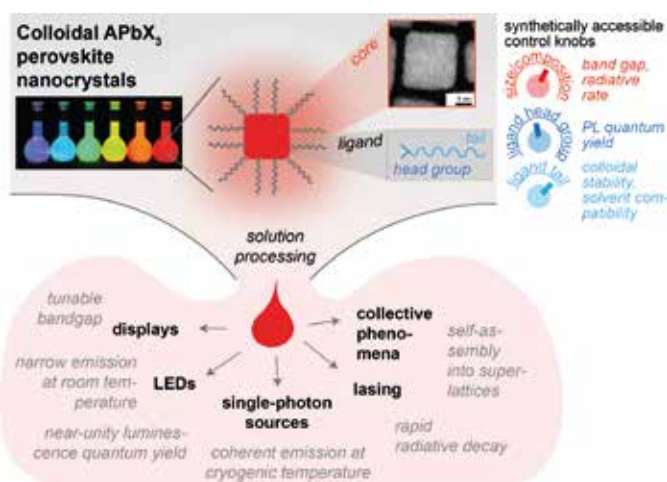


Figure 2. Scheme of a perovskite solar cell structure and functioning principle.

on the position of these layers in the stack and on their morphology: direct mesoscopic, triple-mesoscopic, direct planar and inverted planar.

Progress in PCE has been driven by multiple means such as chemistry and interface layers engineering [3].

The perovskite chemical composition is important. The A, B, X components can be modulated to increase the stability and adjust the optical bandgap. The composition of the precursor solution, including the use of additives and the employed organic solvent, is



Colloidal metal-halide perovskite nanocrystals (NCs), also called "quantum dots", are recently developed nanoscale versions of their intriguing parent bulk semiconductors. Like other colloidal semiconductor (e.g. Cd or Pb chalcogenide) NCs, these perovskite NCs consist of a small inorganic core (typically between 4 nm and 50 nm in size) capped with organic ligands (see schematic). While the size and composition of the NC core determine the degree of quantum (size and dielectric) confinement, providing the synthetic chemist a convenient handle to fine-tune e.g. the bandgap, exciton binding energy, and (non-) radiative rates, the ligands fulfill a multitude of roles: first, the ligand tail maintains colloidal stability in various solvents, enabling access to a large range

of solution-processing approaches for sample handling and device fabrication; second, the ligand head groups provide electronic passivation of the semiconductor core, yielding trap-free semiconductors with near-unity PL quantum yields; and third, the ligand length and coverage can be utilized to control the self-assembly of NCs into NC superlattices, or the separation to a neighboring charge/energy donor or acceptor. In the few years since their first colloidal synthesis [5], perovskite NCs have already turned into a commercial product (<https://avantama.com/>), and have demonstrated ultra-narrow PL at room temperature, low lasing thresholds, as well as bright and coherent single-photon emission at cryogenic temperatures [6]. Given that many researchers and companies are still joining this young and exciting field, the next breakthrough in fundamental science and/or applications is likely just around the corner.

Schematic: Colloidal APbX₃ perovskite nanocrystals are comprised of a size- and composition-tunable perovskite core capped by organic ligands, hereby offering a multitude of synthetically very accessible control knobs to engineer structural and optical properties for a range of solution-processed optoelectronic devices. The photograph is adapted with permission from Nano Lett. **15-6**, 3692 (2015). Copyright 2015 American Chemical Society. The TEM image is reprinted with permission from ACS Cent. Sci. **7-1**, 135 (2021). Copyright 2020 American Chemical Society.

very important to control the final properties of the layer (homogeneity, crystallinity, defect density...). The various steps of the preparation of the perovskite layer, including an antisolvent dripping step, the deposition speed, the annealing temperature, and its duration, have been studied and optimized for reaching high performance. The targeted final morphology is a monolithic structure in which each perovskite grain of the polycrystalline layer is contacted by the ETL on one side and by the HTL on the other side. The interfaces between these layers have been the subject of chemical treatment for energy band level adjustment and defect passivation because defects are at the origin of charge recombination and performance losses. Due to the mild temperature used for the layer annealing, PSCs can be prepared on lightweight low-cost plastic substrates compatible with a roll-to-roll process for large-scale production.

The stability concern has led to important research on the reduction of the dimensionality of the perovskites and on the preparation of 2D/3D perovskite mixtures. Perovskite can be integrated into tandem solar cells to increase their maximum theoretical PCE limit. Rather low bandgap perovskites are prepared by mixing Pb and Sn B-cation while the bandgap is increased by partly substituting I for Br. Full-perovskite double-junction solar cells achieve a maximum PCE above 26.4%. Perovskite solar cells are not only a competitor to silicon but, also, an ancillary technology since perovskite can provide the top cell with a bandgap larger and complementary to that of crystalline silicon in tandem devices. This research direction has raised a large amount of effort and funds in recent years. The current record efficiency is 31.3%.

LEDs

The recent technological developments in various application areas such as automotive, smartphones, TV, or flexible screens revealed some limitations of the widely used inorganic semiconductors. Therefore, the community has moved towards alternative technologies that also consider the materials' availability. Among the candidates, organic electronics is a suitable way to achieve new devices. It is particularly true for optoelectronic components. However, the all-organic approach does not provide the same performance as purely inorganic semiconductors due to the moderate transport properties of the charge carriers in these materials. In this context, halide perovskites are relevant materials, especially the low dimensional ones (2D, 1D, 0D) which present stronger excitonic effects than the bulk [4]. In particular, perovskite nanocrystals (NCs, see inset), respond well to the technological need for easily exploitable semiconductors, synthesized with facile and cheap processes, as conformable as the all-organic, with performances equivalent to classical semiconductors [5]. Perovskite-based NCs are a viable Cd-free alternative for display applications. The main advantages of perovskite-based NCs are their facile and low-cost synthesis, high photoluminescence (PL) quantum yields between 50% and ●●●



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SINGLE-PHOTON SOURCES

Halide perovskites have also made inroads into another area less known to the general public but from which we can hope for very interesting future applications. This is the field of quantum optics and quantum information. Indeed, from the first synthesis of NCs it has been shown that the emission of an isolated perovskite NC was carried out photon by photon. That is a property specific to two-level systems or atomic systems that also appears under some conditions on individual three-dimensional quantum confined semiconductors. It is also very desired in quantum cryptography to design single-photon sources because as opposed to attenuated coherent sources, a single-photon source allows an improvement in performance in terms of maximum reachable distance for

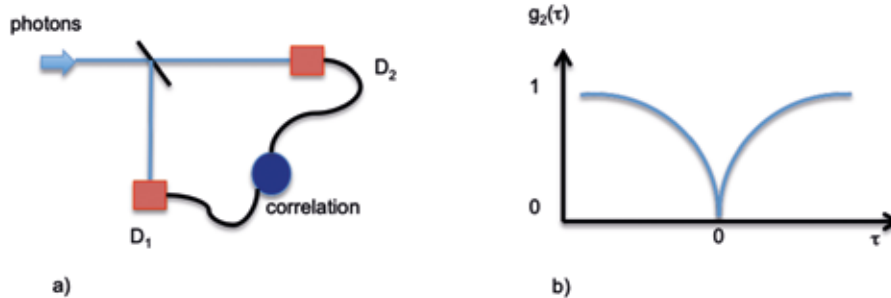


Figure 3. a) Scheme of a Hanbury-Brown and Twiss experiment: a photon stream is incident in a beam splitter, D_1 and D_2 are single-photon counting detectors, the correlator gives $g_2(\tau)$, the conditional probability of detecting a second photon at time $t + \tau$ in detector D_2 , given the detection of a photon at t from detector D_1 . b) $g_2(\tau)$ ideal curve.

a given security level.

Quantum-cryptography protocols are based on the coding of quantum states (e.g., the polarization of a single photon) and the sharing between two interlocutors of a secret key in the form of a random series via a quantum channel (e.g. an optical fiber). The laws of quantum mechanics ensure the ability of the two interlocutors to detect the presence of a spy on the transmission line. Moreover, the quantum interferences between states of one photon can also be applied to make photonic logic gates to be inserted in future quantum computers.

Whatever the application of the single-photon sources, the main characteristics of these sources are as follows:

- Ideally, such source should emit one and only one photon for each trigger signal in a defined mode of the electromagnetic field. As already seen in Section LEDs, perovskite NCs show a highly efficient PL at room temperature. That is combined with a reduced intermittence or “blinking” of the single-photon emission due to the fluctuant electrostatic environment of NCs.
- Ideal single-photon sources show statistics characterized by a second-order correlation function at

zero time $g_2(0)=0$. This function characterizes the probability to detect another photon at the same time that one photon was previously detected at $t = 0$ in a Hanbury-Brown and Twiss experiment (Figure 3). For CsPbI₃ nanocrystals, $g_2(0)$ values as low as 0.02 have been reported [7];

- A high repetition rate (tens of MHz at room temperature).
- Easy and reliable use. The stability of NCs against moisture or irradiation with intense light needs to be improved.
- Finally, a good collection efficiency. As in the case of LEDs, efficient collection of the emitted light, mostly trapped by total internal reflection in the material, is a true challenge.

LASERS/PHOTONICS

The former sections highlighted and illustrated the key advantages of halide perovskites for the next generations of photonic and opto-electronic devices. However, advanced photon control is necessary to further control their performance and to integrate advanced functionalities. In particular, tight control of the spectral, spatial and angular properties of the emitted light can be achieved through the integration of wavelength scale structures like periodic gratings, metasurfaces, or other kind of nanophotonic patterns. This is generally achieved by a direct patterning of the halide perovskite layer, using processes inspired by nanoimprint or hot embossing. Such an advanced photonic control could lead to major breakthroughs in devices like LEDs or single photon sources, where

managing the radiation pattern can be of prime importance. Using such properties, light-emitting devices can exhibit characteristics suited to applications like visible light communication (VLC). Integrating such nanopatterns can also assist light trapping in photovoltaic solar cells, both in the case of single junction solar cell and tandem devices [8].

Additionally, advanced photon control is necessary to reach regimes like laser emission or strong coupling. To reach this goal, it is necessary to integrate wavelength-scale photonic patterns to constitute the needed optical resonator. During these past years, low threshold laser emission was demonstrated under optical pumping in simple structures including periodic grating (1D or 2D), metasurfaces, or related patterns. Considering the very high optical gain available in such media, laser emission could even be achieved in single nanostructures, simultaneously providing the optical gain and the cavity. Beyond these important demonstrations, a key challenge is to reach laser emission under electrical injection, which could be achievable thanks to strategies circumventing the Joule heating, electric field-induced quenching, charge injection imbalance and Auger recombination.

CONCLUSION

In summary, hybrid halide perovskites are a new class of semiconductors showing an incredible set of physical properties, which are rarely united in the same material. These physical properties can be easily tuned and adapted to the intended application by modifying the composition of the material. Additionally, these materials are solution-processed, with soft conditions of temperature and pressure, and contain earth-abundant components. However, some important challenges remain to be solved for this class of materials: the presence of lead and the so far limited operational stability against environmental parameters such as humidity and intense light. If the presence of lead can presumably be treated by implementing recyclability if necessary, the stability remains a major problem as the device stability is, at present, not yet sufficient for commercialization, even if tremendous progress has been made in the past few years. Some efforts are still needed, the solution to this problem will probably come from the major advantage of this class of materials: its chemical flexibility. ●

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