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Spontaneous Silver Doping and Surface Passivation of CsPbI₃ Perovskite Active Layer Enable Light-Emitting Devices with an External Quantum Efficiency of 11.2%

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Abstract

Lead halide perovskite nanocrystals are currently under intense investigation as components of solution-processed light-emitting devices (LEDs). We demonstrate LEDs based on Ag doped-passivated CsPbI₃ perovskite nanocrystals with external quantum efficiency of 11.2% and an improved stability. Ag and trilayer MoO₃/Au/MoO₃ structure were used as cathode and anode, respectively, which reduce the electron injection barrier and ensure the high transparency and low resistance of the anode. Silver ions diffuse into perovskite film from the Ag electrode, as confirmed by the elemental mapping, the presence of Ag 3d peaks in the X-ray photoelectron spectrum, and the peak shift in the X-ray diffraction patterns of CsPbI₃. In addition to doping, silver ions play the beneficial role of passivating surface defect states of CsPbI₃ nanocrystals, which results in increased photoluminescence quantum yield, elongated emission lifetime, and improved stability of perovskite films.

Graphical Abstract

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ASSOCIATED CONTENT

Supporting Information

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Experimental details on materials synthesis, device fabrication, and characterizations; EQEs for 26 Agdoped CsPbI₃ NC-based LEDs; Cs 3d XPS spectra; TEM images; elemental mapping; EDX spectrum; crosssectional SEM images; stability tests for Ag- and ITO-based devices; and optical spectra (PDF)

Notes

The authors declare no competing financial interest.

Lead halide perovskite nanocrystals (NCs) have attracted significant attention as components of solution-processed light-emitting devices (LEDs) because of their desirable optical characteristics such as high photoluminescence quantum yield (PL QY), narrow emission, and wide color range.^{1–5} As a result of the rapid progress in improving device architectures and compositional engineering, the external quantum efficiencies (EQE) of the perovskite NC-based LEDs have exceeded 8%.^{6,7} However, there is still a room for improvement of these devices as compared with LEDs utilizing traditional II–VI semiconductor quantum dots, where best EQE values currently reach 20%.^{8,9}

Recently, metal ion doping has been applied as a tool to tune optical and electronic properties of lead halide perovskite materials.¹⁰ A variety of dopant ions such as Mn^{2+} , Zn^{2+} , Cd^{2+} , Sn^{2+} , Bi^{3+} , and lanthanide ions have been shown to improve the stability and PL QY of perovskites, tune their Fermi level, and eventually change conductivity characteristics from n-type to p-type.^{11–15} Several studies also reported improvements of EQEs of CsPbBr_3 NC-based LEDs utilizing the suitable metal ion doping: namely from 0.8% to 1.4% via Mn^{2+} doping;¹⁶ from 1.0% to 4.1% via Sn^{4+} doping;¹⁷ and from 1.6% to 4.4% via Ce^{3+} doping.¹⁸

In this work, we have utilized the Ag cathode to reduce the electron injection barrier in the CsPbI_3 perovskite NC-based LEDs, as compared with similar devices utilizing traditional ITO cathode. More importantly, spontaneous doping of Ag^+ ions into the light-emitting layer of CsPbI_3 perovskite NCs has been realized, as confirmed by the elemental mapping, X-ray photoelectron spectroscopy (XPS), and the X-ray diffraction (XRD) studies. When the ITO cathode was replaced with Ag, the peak EQE of CsPbI_3 NC-based LEDs was enhanced from 7.3 to 11.2% and the stability of nonencapsulated devices in nitrogen and ambient atmosphere was improved. We discuss in detail beneficial effects of Ag doping and Ag^+ ion surface defect passivation on the PL QY and stability of CsPbI_3 NCs and LED performance characteristics of the respective devices below.

Figure 1a shows the optical absorption and PL spectra of CsPbI_3 NCs in toluene. The absorption and PL peaks are located at 677 and 690 nm, respectively. The NC solution exhibits bright red emission (PL QY over 60%) under 365 nm excitation, with a high color purity [full width at half-maximum (fwhm) equals 36 nm]. The XRD pattern of a CsPbI_3 NC

film on a quartz substrate (Figure 1b) matches the reference pattern of the bulk cubic CsPbI₃. A transmission electron microscopy (TEM) image of CsPbI₃ NCs is given in the inset of Figure 1b and shows the presence of rather monodisperse cubic-shaped NCs with an edge length of 10–12 nm.

Two kinds of multilayer LEDs have been fabricated and compared in this work; the LEDs comprised a patterned ITO or Ag cathode, ZnO NC/polyethylenimine (PEI) bilayer as the electron-transporting layer (ETL), CsPbI₃ NC film as the emitting layer, 4,4,4''-tris(carbazol-9-yl)triphenylamine (TCTA) film as the hole-transporting layer (HTL), and MoO₃/Au or MoO₃/Au/MoO₃ as the anode, as presented in Figure 2a. The energy level diagram for all functional layers of these devices is given in Figure 2b. The wide bandgap ZnO NC film was chosen as ETL and at the same time served as a holeblocking layer (HBL) because of its high electron mobility, excellent optical transparency, and the deep-lying VBM (valence band maximum, -7.2 eV).¹⁹ The TCTA film was chosen as HTL and at the same time served as an electron-blocking layer (EBL) because of its suitable highest occupied molecular orbital (HOMO, -5.7 eV) and low electron affinity (-2.3 eV).²⁰ The combination of ZnO HBL and TCTA EBL sandwiched around the CsPbI₃ NC emitting layer allowed for confinement of injected charge carriers resulting in an efficient radiative recombination. The PEI interlayer not only lowered the work function of cathode contacts but also helped to maintain charge neutrality of CsPbI₃ NC emitters and preserve their superior emissive properties.¹⁹

Efficient LEDs require electrodes with both high transparency and low resistance. Metal films are highly conductive but inherently opaque to visible light; therefore, when using them as transparent electrodes, the layer thickness should be low (typically less than 20 nm) to ensure transparency.²¹ Metal oxide/metal/metal oxide trilayer structures, on the other hand, are widely employed in LEDs for achieving both high transparency and low resistance.²² We thus tested different configurations of the cathode and anode trilayers to ensure the fulfillment of the above-mentioned conditions. Because our goal was to replace ITO with Ag, we first attempted to deposit a ZnO-1/Ag/ZnO-2 trilayer structure on the substrate. However, in order to ensure the charge transporting balance, the thickness of the top ZnO-2 film must be at least 40 nm, which hardly provides high transparency. Moreover, as ZnO NC films were deposited from solution, it was difficult to ensure a homogeneous surface morphology and proper grain connectivity if keeping the ZnO-1 layer ultrathin (around 10 nm). For these two reasons, instead of producing LEDs with a transparent cathode, we decided to optimize the anode side to make it transparent, using a MoO₃-1/Au/MoO₃-2 (MAM) trilayer structure. The MoO₃-1 layer was situated between the TCTA and the Au film and served as the hole injection layer. When device parameters of the ITO-based CsPbI₃ NC LEDs were systematically checked, an optimum thickness of 20 nm for the MoO₃-1 layer was determined for the best-performing devices. A thin 10 nm Au layer was employed to ensure high transparency and at the same time good conductivity of the MAM structure. The MoO₃-2 layer was deposited on top of the Au layer to reduce the light reflection at the Au/air interface.²² Figure 2c shows the two-dimensional optical transmission map of MAM layers with different MoO₃-2 thicknesses, indicating that the transmittance reached the highest value for the MoO₃-2 layer thickness of 25 nm. As shown in Figure 2d an enhancement in transmission ($T = T_{25\text{nm}} - T_{0\text{nm}}$) of about 10% was

achieved in the spectral range of 450–750 nm. In particular, the transmittance of the MAM structure at 690 nm, which is the peak position of the CsPbI₃ electroluminescence (EL), increased from 57% to 67% with the 25 nm MoO₃-2 film. By employing the four-point probe method, we measured the resistance of the optimized MAM structure to be 15 Ω sq⁻¹, which is thus suitable to serve as an LED anode.

The average peak EQE of the multilayer LEDs increased from 7.3 to 11.2% upon replacing the ITO cathode with Ag (Figure 2e). The insets in Figure 2e show photographs of working devices with Ag and ITO cathodes. The reproducibility of the EQEs of the devices with Ag cathode was high: as shown in Figure S1, an average peak EQE of 11.2% from 26 devices was achieved. Two best-performing devices exhibited an EQE of 12.1%, which is to the best of our knowledge the highest efficiency in CsPbI₃ perovskite NC-based LEDs. Voltage-dependent variations of current density and luminance for the devices employing ITO and Ag cathodes are shown in Figure 2f. Even though the ITO film has much higher transmittance (95%) at the EL peak position than the MAM trilayer (67%), as shown in the inset of Figure 2d we found the peak brightness of LEDs with Ag cathode (1106 cd m⁻²) to be more than double that of the ITO-based device (455 cd m⁻²), and the current density of the Ag-based device was lower than that of the ITO-based device under the same voltage, which demonstrates that higher charge injection efficiency was achieved benefiting from the reduction of the electron injection barrier.

For the purpose of identifying the chemical states of constituting elements in the CsPbI₃ NC layer (eventually doped with Ag), X-ray photoelectron spectroscopy (XPS) spectra were taken from Ag/ETL/CsPbI₃ and ITO/ETL/CsPbI₃ films. Panels a, b, and c of Figure 3 show XPS spectra for Pb, I, and Ag elements, respectively, all calibrated with C 1s. No peak shift was observed for Cs 3d (Figure S2), while Pb 4f and I 3d peaks shifted to higher binding energy in Ag/ETL/CsPbI₃ as compared to ITO/ETL/CsPbI₃ films: for Pb 4f (Figure 3a), the peak shifted from 143.6 to 143.8 eV, and for I 3d (Figure 4b), it shifted from 631.1 to 632.2 eV. These shifts evidence the changes in chemical bonding between the lead cation and iodide anion in CsPbI₃,²³ which are associated with the influence of the bottom electrodes (Ag vs ITO). Moreover, as shown in Figure 3c, the Ag 3d peaks appeared for the Ag/ETL/CsPbI₃ sample, while no In 3d peaks (In₂O₃:SnO₂ $\approx$ 9:1 in ITO) have been detected in the ITO/ETL/CsPbI₃ sample. Ag 3d spectra consist of two peaks at 374.1 eV (3d_{3/2}) and 368.1 eV (3d_{5/2}), which can be further deconvoluted into subpeaks at 374.1 and 373.3 eV, and 368.1 and 367.6 eV, corresponding to 3d_{3/2} and 3d_{5/2} binding energies, respectively. The peaks located at 374.1 and 368.1 eV can be assigned to metal Ag⁰, while the 373.3 and 367.6 eV peaks are assigned to Ag⁺.²⁴

The presence of Ag 3d peaks in the XPS spectra indicates that silver ions diffused from the underlying Ag electrode into the CsPbI₃ NC film. When the Ag-based LED was fabricated, a 100 nm Ag film was first deposited onto the substrate via thermal evaporation, followed by the ZnO film deposition in air and annealing at 120 °C for 10 min. Such a treatment in air may lead to formation of a thin oxide layer of Ag₂O between the Ag cathode and the ZnO film, which serves as a source of Ag⁺ ions diffusing into the perovskite CsPbI₃ film.²⁵ Upon silver ion diffusion, some may form AgI through reaction with I⁻ ions at the CsPbI₃ NC surface,²⁶ while others may enter the crystalline lattice of the perovskite. As AgI can readily

decompose into Ag^0 under illumination,^{27–29} it may produce some metallic Ag on the CsPbI_3 NC surface.

The shifts of the peak positions for Pb 4f and I 3d to higher binding energy in the Ag/ETL/ CsPbI_3 samples (Figure 3a,b) and the presence of Ag^+ 3d peaks (Figure 3c) demonstrate that silver ions have become inserted into the crystal structure of the perovskite. This is further supported by the shift of the peak positions in the XRD patterns, shown in Figure 3d. For Ag/ETL/ CsPbI_3 films, Ag^+ ions entered the crystal lattice, as exemplified by the shifts of all XRD peaks to higher angles as compared with ITO/ETL/ CsPbI_3 .³⁰ This happens because of the shrinkage of the CsPbI_3 lattice volume upon the insertion of some Ag^+ ions (ionic radius 1.26 Å) taking place of Cs^+ (ionic radius 1.67 Å).³¹

To further confirm that the diffusion of silver ions into the perovskite NC film does take place, CsPbI_3 NCs from the Ag/ETL/ CsPbI_3 NC film were redissolved into toluene to carry out TEM, elemental mapping, and energy-dispersive X-ray (EDX) elemental analysis. As shown in Figure S3a, the redissolved NCs mostly maintain the cubic morphology characteristic to CsPbI_3 nanoparticles. From the elemental mapping (Figure S3b–f), it can be seen that the Ag element coexists with the Cs, Pb, and I elements from the original perovskite NCs, and all the elements are rather equally distributed. The Ag content was estimated to be 6% from the EDX data. Furthermore, the cross-sectional scanning electron microscopy (SEM) images combined with elemental mapping were collected from the Ag/ETL/ CsPbI_3 NC film and provided direct evidence for the diffusion of silver ions into the CsPbI_3 NCs. As shown in Figure S4, while Cs, Pb, and I ions are almost uniformly distributed over the film profile, the silver content gradually decreases over the distance away from the Ag electrode.

The PL stability of drop-casted CsPbI_3 NC films stored at the ambient conditions was compared (Figure 4a). The PL QY of ITO/ CsPbI_3 samples decreased to ~50% of their initial value within 24 h, while the PL QY of Ag/ETL/ CsPbI_3 samples maintained 80% of their initial value after 48 h. Note that for the ITO-based samples, the CsPbI_3 film stability was enhanced after introducing an ETL (ZnO/PEI), which is due to the PEI passivation of the perovskite NC surface defects.¹⁹ For the Ag-based samples in contrast, the CsPbI_3 film stability decreased after introducing an ETL, which is due to the reduced number of Ag^+ ions able to diffuse from the underlying Ag substrate. The improved stability of the CsPbI_3 NC film may originate from the existence of Ag and/or AgI absorbed on the surface of CsPbI_3 NCs, which partially stabilize perovskite NCs from moisture and light irradiation.^{32–34} To confirm this hypothesis, we dissolved the CsPbI_3 NCs out of Ag/ETL/ CsPbI_3 films using toluene and collected their TEM images. It was found that most of the CsPbI_3 perovskite NCs are covered with dark nanoparticles, as shown in Figure S5a. The elemental mapping characterization (Figure S5b–f) has shown that the dark round particles are either Ag or AgI, which indicates that the diffused silver ions are anchored on the perovskite NC surface in the Ag/ETL/ CsPbI_3 films in the form of Ag and/or AgI.

Benefiting from the enhanced CsPbI_3 NC film stability, the EL stability of the respective devices has been also improved.^{35–37} As shown in Figure 4b, the EL intensity of ITO-based CsPbI_3 LEDs decreased to ~50% of their initial value in 5 days, while the EL intensity of

Ag-based CsPbI₃ LEDs maintained 80% of their initial value after 10 days of storage in a glovebox under nitrogen. In addition, the EL stability of both devices under continuous operation at a constant voltage of 2.5 V was tested under ambient conditions and in the air-free glovebox atmosphere. As shown in Figure S6, the Ag-based devices show better operation stability than ITO-based device when tested in both conditions.

In addition to the observed improvements in stability, brightness, and EQE, the Ag-based devices also exhibited stronger PL than ITO-based ones. The absolute PL QYs of ITO/ETL/CsPbI₃, Ag/ETL/CsPbI₃, and Ag/CsPbI₃ were 60%, 70%, and 81%, respectively, while their PL spectral profiles were the same (Figure S7). The PL lifetime of the Ag/ETL/CsPbI₃ film was also longer than that of the ITO/ETL/CsPbI₃, as shown in Figure 4c. The average PL lifetime of the cathode/ETL/CsPbI₃ structure increased from 4.8 to 8.8 ns when ITO was replaced with Ag. Note that when we increased the amount of Ag⁺ ions which diffused into the perovskite lattice by removing the ETL, the PL decay transformed from biexponential to monoexponential (Figure 4c), indicating the efficient passivation of surface defects of CsPbI₃ NCs by Ag⁺ ions.^{38,39} The average PL lifetime of Ag/CsPbI₃ samples increased to 15.4 ns. The elongated emission lifetime and improved PL QY of Ag/ETL/CsPbI₃ NC films ensure the higher brightness and EQE compared with that of ITO/ETL/CsPbI₃-based devices.

In order to further confirm the beneficial effect of silver on CsPbI₃ NCs, the following control experiment was performed. As shown in Figure S8, we added AgC₂H₃O₂-OLA solution (equivalent volume with different Ag⁺ concentration) into CsPbI₃ NC solution (equivalent volume with the same concentration). The band tail states in absorption spectra disappeared (Figure S8a) and the PL intensity increased (Figure S8b) when Ag⁺ ions were introduced, demonstrating the passivation of surface defects of CsPbI₃ NCs.^{40,41} In addition, all CsPbI₃ NCs treated with silver ions exhibited improved stability, as shown in Figure S8c. These results provide additional evidence that silver ions play an important role in improving optical characteristics of CsPbI₃ NCs, thus enhancing the LED performance.

Both hole and electron transport properties of multilayer LEDs were enhanced, as seen from comparison of the respective “electron-only” and “hole-only” devices. For the electron-only devices, a structure of (ITO or Ag)/ZnO/CsPbI₃ NC/LiF/Al was employed. For the hole-only devices, a structure of (ITO or Ag)/PEDOT:PSS/CsPbI₃ NC/TCTA/MoO₃/Au was employed. As shown in Figure 4d, the currents of all Ag-based devices were higher than that of ITO-based devices.

In conclusion, we have developed a method of simultaneous doping and surface passivation of CsPbI₃ NC films with silver. Some Ag⁺ ions substitute Cs⁺ ions in the lattice structure of perovskites, which leads to their stabilization; passivation of CsPbI₃ NC surface with Ag⁺ ions converts nonradiative trap states to radiative states, resulting in the enhancement of PL QY. In the LEDs utilizing Ag-doped CsPbI₃ NCs as emitting layer, Ag was chosen as a cathode to reduce the electron injection barrier, and trilayer MoO₃/Au/MoO₃ structure served as an anode to ensure the high transparency and good conductivity. As a result, the charge carrier transport properties of CsPbI₃ films have been improved, which led to

cumulative enhancement of the performance of Ag-doped CsPbI₃ NC-based LEDs employing the silver cathodes, with EQE averaging 11.2%.

Supplementary Material

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REFERENCES

- (1). Protesescu L; Yakunin S; Bodnarchuk MI; Krieg F; Caputo R; Hendon CH; Yang RX; Walsh A; Kovalenko MV Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* 2015, 15, 3692–3696. [PubMed: 25633588]
- (2). Li X; Wu Y; Zhang S; Cai B; Gu Y; Song J; Zeng H Quantum Dots: CsPbX₃ Quantum Dots for Lighting and Displays: Room-Temperature Synthesis, Photoluminescence Superiorities, Underlying Origins and White Light-Emitting Diodes. *Adv. Funct. Mater.* 2016, 26, 2435–2445.
- (3). Hu F; Yin C; Zhang H; Sun C; Yu WW; Zhang C; Wang X; Zhang Y; Xiao M Slow Auger Recombination of Charged Excitons in Nonblinking Perovskite Nanocrystals without Spectral Diffusion. *Nano Lett.* 2016, 16, 6425–6430.
- (4). Huang H; Polavarapu L; Sichert JA; Susha AS; Urban AS; Rogach AL Colloidal Lead Halide Perovskite Nanocrystals: Synthesis, Optical Properties and Applications. *NPG Asia Mater.* 2016, 8, e328.
- (5). Yin C; Chen L; Song N; Lv Y; Hu F; Sun C; Yu WW; Zhang C; Wang X; Zhang Y; et al. Bright-Exciton Fine-Structure Splittings in Single Perovskite Nanocrystals. *Phys. Rev. Lett.* 2017, 119, 026401. [PubMed: 28753331]
- (6). Chiba T; Hoshi K; Pu YJ; Takeda Y; Hayashi Y; Ohisa S; Kawata S; Kido J High Efficiency Perovskite Quantum-Dot Light-Emitting Devices by Effective Washing Process and Interfacial Energy Level Alignment. *ACS Appl. Mater. Interfaces* 2017, 9, 18054–18060. [PubMed: 28485139]
- (7). Yan F; Xing J; Xing G; Quan L; Tan ST; Zhao J; Su R; Zhang L; Chen S; Zhao Y; et al. Highly Efficient Visible Colloidal Lead-Halide Perovskite Nanocrystal Light-Emitting Diodes. *Nano Lett.* 2018, 18, 3157–3164. [PubMed: 29608317]
- (8). Dai X; Zhang Z; Jin Y; Niu Y; Cao H; Liang X; Chen L; Wang J; Peng X Solution-Processed, High-Performance Light-Emitting Diodes Based on Quantum Dots. *Nature* 2014, 515, 96–99. [PubMed: 25363773]
- (9). Zhang H; Sun X; Chen S Light-Emitting Diodes: Over 100 cd A⁻¹ Efficient Quantum Dot Light-Emitting Diodes with Inverted Tandem Structure. *Adv. Funct. Mater.* 2017, 27, 1700610.
- (10). Swarnkar A; Ravi VK; Nag A Beyond Colloidal Cesium Lead Halide Perovskite Nanocrystals: Analogous Metal Halides and Doping. *ACS Energy Lett.* 2017, 2, 1089–1098.
- (11). Begum R; Parida MR; Abdelhady AL; Murali B; Alyami NM; Ahmed GH; Hedhili MN; Bakr OM; Mohammed OF Engineering Interfacial Charge Transfer in CsPbBr₃ Perovskite Nanocrystals by Heterovalent Doping. *J. Am. Chem. Soc.* 2017, 139, 731–737. [PubMed: 27977176]

- (12). van der Stam W; Geuchies JJ; Altantzis T; van den Bos KHW; Meeldijk JD; Van Aert S; Bals S; Vanmaekelbergh D; de Mello Donega C Highly Emissive Divalent-Ion-Doped Colloidal $\text{CsPb}_{1-x}\text{M}_x\text{Br}_3$ Perovskite Nanocrystals through Cation Exchange. *J. Am. Chem. Soc* 2017, 139, 4087–4097. [PubMed: 28260380]
- (13). Liu W; Lin Q; Li H; Wu K; Robel I; Pietryga JM; Klimov VI Mn^{2+} -Doped Lead Halide Perovskite Nanocrystals with Dual-Color Emission Controlled by Halide Content. *J. Am. Chem. Soc* 2016, 138, 14954–14961. [PubMed: 27756131]
- (14). Pan G; Bai X; Yang D; Chen X; Jing P; Qu S; Zhang L; Zhou D; Zhu J; Xu W; et al. Doping Lanthanide into Perovskite Nanocrystals: Highly Improved and Expanded Optical Properties. *Nano Lett.* 2017, 17, 8005–8011. [PubMed: 29182877]
- (15). Zhu J; Yang X; Zhu Y; Wang Y; Cai J; Shen J; Sun L; Li C Room-Temperature Synthesis of Mn-Doped Cesium Lead Halide Quantum Dots with High Mn Substitution Ratio. *J. Phys. Chem. Lett* 2017, 8, 4167–4171. [PubMed: 28819974]
- (16). Zou S; Liu Y; Li J; Liu C; Feng R; Jiang F; Li Y; Song J; Zeng H; Hong M; et al. Stabilizing Cesium Lead Halide Perovskite Lattice through Mn (II)-Substitution for Air-Stable Light-Emitting Diodes. *J. Am. Chem. Soc* 2017, 139, 11443–11450. [PubMed: 28756676]
- (17). Wang HC; Wang W; Tang AC; Tsai HY; Bao Z; Ihara T; Yarita N; Tahara H; Kanemitsu Y; Chen S High-Performance Novel $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ Perovskite Quantum Dots for Highly-Efficient Light-Emitting Diodes. *Angew. Chem. Int. Ed* 2017, 56, 13650–13654.
- (18). Yao J; Ge J; Han BN; Wang KH; Yao HB; Yu HL; Li JH; Zhu BS; Song J; Chen C; et al. Ce^{3+} -Doping to Modulate Photoluminescence Kinetics for Efficient CsPbBr_3 Nanocrystals Based Light-Emitting Diodes. *J. Am. Chem. Soc* 2018, 140, 3626–3634. [PubMed: 29341604]
- (19). Zhang X; Sun C; Zhang Y; Wu H; Ji C; Chuai Y; Wang P; Wen S; Zhang C; Yu WW Bright Perovskite Nanocrystal Films for Efficient Light-Emitting Devices. *J. Phys. Chem. Lett* 2016, 7, 4602–4610. [PubMed: 27758105]
- (20). Wang J; Wang N; Jin Y; Si J; Tan Z-K; Du H; Cheng L; Dai X; Bai S; He H; et al. Interfacial Control Toward Efficient and Low-Voltage Perovskite Light-Emitting Diodes. *Adv. Mater* 2015, 27, 2311–2316. [PubMed: 25708283]
- (21). Yambem SD; Ullah M; Tandy K; Burn PL; Namdas EB ITO-Free Top Emitting Organic Light Emitting Diodes with Enhanced Light Out-Coupling. *Laser Photonics Rev.* 2014, 8, 165–171.
- (22). Wu H; Zhang Y; Zhang X; Lu M; Sun C; Bai X; Zhang T; Sun G; Yu WW Fine-Tuned Multilayered Transparent Electrode for Highly Transparent Perovskite Light-Emitting Devices. *Adv. Electron. Mater* 2018, 4, 1700285.
- (23). Nam JK; Chai SU; Cha W; Choi YJ; Kim W; Jung MS; Kwon J; Kim D; Park JH Potassium Incorporation for Enhanced Performance and Stability of Fully Inorganic Cesium Lead Halide Perovskite Solar Cells. *Nano Lett.* 2017, 17, 2028–2033. [PubMed: 28170276]
- (24). Lee S; Park JH; Bo RL; Jung ED; Yu JC; Nuzzo DD; Friend RH; Song MH Amine-Based Passivating Materials for Enhanced Optical Properties and Performance of Organic-Inorganic Perovskite in Light-Emitting Diodes. *J. Phys. Chem. Lett* 2017, 8, 1784–1792. [PubMed: 28378585]
- (25). Chen CW; Hsieh PY; Chiang HH; Lin CL; Wu HM; Wu CC Top-Emitting Organic Light-Emitting Devices Using Surface-Modified Ag Anode. *Appl. Phys. Lett* 2003, 83, 5127–5129.
- (26). Back H; Kim G; Kim J; Kong J; Kim TK; Kang H; Kim H; Lee J; Lee S; Lee K Achieving Long-Term Stable Perovskite Solar Cells via Ion Neutralization. *Energy Environ. Sci* 2016, 9, 1258–1263.
- (27). Lin H; Cao J; Luo B; Xu B; Chen S Synthesis Of Novel Z-Scheme AgI/Ag/AgBr Composite with Enhanced Visible Light Photocatalytic Activity. *Catal. Commun* 2012, 21, 91–95.
- (28). Zheng Z; Chen C; Bo A; Zahir FS; Waclawik ER; Zhao J; Yang D; Zhu H Visible-Light-Induced Selective Photocatalytic Oxidation of Benzylamine into Imine over Supported Ag/AgI Photocatalysts. *ChemCatChem* 2014, 6, 1210–1214.
- (29). Yu C; Wei L; Zhou W; Chen J; Fan Q; Liu H Enhancement of the Visible Light Activity and Stability of Ag_2CO_3 by Formation of $\text{AgI/Ag}_2\text{CO}_3$ Heterojunction. *Appl. Surf. Sci* 2014, 319, 312–318.

- (30). Akkerman QA; Meggiolaro D; Dang Z; De Angelis F; Manna L Fluorescent Alloy $\text{CsPb}_x\text{Mn}_{1-x}\text{I}_3$ Perovskite Nanocrystals with High Structural and Optical Stability. *ACS Energy Lett.* 2017, 2, 2183–2186. [PubMed: 29142911]
- (31). Swarnkar A; Mir WJ; Nag A Can B-Site Doping or Alloying Improve Thermal- and Phase-Stability of All-Inorganic CsPbX_3 (X = Cl, Br, I) Perovskites? *ACS Energy Lett.* 2018, 3, 286–289.
- (32). Luo B; Pu YC; Lindley SA; Yang Y; Lu L; Li Y; Li X; Zhang JZ Organolead Halide Perovskite Nanocrystals: Branched Capping Ligands Control Crystal Size and Stability. *Angew. Chem* 2016, 128, 9010–9014.
- (33). Yang D; Li X; Zeng H Surface Chemistry of All Inorganic Halide Perovskite Nanocrystals: Passivation Mechanism and Stability. *Adv. Mater. Interfaces* 2018, 5, 1701662.
- (34). Krieg F; Ochsenbein ST; Yakunin S; ten Brinck S; Aellen P; Süess A; Clerc B; Guggisberg D; Nazarenko O; Shynkarenko Y; et al. Colloidal CsPbX_3 (X = Cl, Br, I) Nanocrystals 2.0: Zwitterionic Capping Ligands for Improved Durability and Stability. *ACS Energy Lett.* 2018, 3, 641–646. [PubMed: 29552638]
- (35). Swarnkar A; Marshall AR; Sanehira EM; Chernomordik BD; Moore DT; Christians JA; Chakrabarti T; Luther JM Quantum Dot-Induced Phase Stabilization of A- CsPbI_3 Perovskite for High-Efficiency Photovoltaics. *Science* 2016, 354, 92–95. [PubMed: 27846497]
- (36). Zou C; Huang CY; Sanehira EM; Luther J; Lin LY Highly Stable Cesium Lead Iodide Perovskite Quantum Dot Light-Emitting Diodes. *Nanotechnology* 2017, 28, 455201. [PubMed: 29039355]
- (37). Sim KM; Swarnkar A; Nag A; Chung DS Phase Stabilized α - CsPbI_3 Perovskite Nanocrystals for Photodiode Applications. *Laser Photonics Rev.* 2018, 12, 1700209.
- (38). Zhou J; Zhu M; Meng R; Qin H; Peng X Ideal CdSe/CdS Core/Shell Nanocrystals Enabled by Entropic Ligands and Their Core Size-, Shell Thickness-, and Ligand-Dependent Photoluminescence Properties. *J. Am. Chem. Soc* 2017, 139, 16556–16567. [PubMed: 29094943]
- (39). Koscher BA; Swabeck JK; Bronstein ND; Alivisatos AP Essentially Trap-Free CsPbBr_3 Colloidal Nanocrystals by Postsynthetic Thiocyanate Surface Treatment. *J. Am. Chem. Soc* 2017, 139, 6566–6569. [PubMed: 28448140]
- (40). Liu M; Voznyy O; Sabatini R; Arquer FPGD; Munir R; Balawi AH; Lan X; Fan F; Walters G; Kirmani AR; et al. Hybrid Organic-Inorganic Inks Flatten the Energy Landscape in Colloidal Quantum Dot Solids. *Nat. Mater* 2017, 16, 258. [PubMed: 27842072]
- (41). Woo JY; Kim Y; Bae J; Kim TG; Kim JW; Lee DC; Jeong S Highly Stable Cesium Lead Halide Perovskite Nanocrystals through in Situ Lead Halide Inorganic Passivation. *Chem. Mater* 2017, 29, 7088–7092.

Figure 1. (a) Absorption (black) and PL (red) spectra of CsPbI₃ NCs in toluene. (b) XRD pattern of the CsPbI₃ NC film on quartz substrate (red); reference pattern for bulk CsPbI₃ is provided in black. Inset in panel b shows the TEM image of CsPbI₃ NCs.

Figure 2.

(a) Schematic diagrams of the CsPbI₃ NC-based LEDs with ITO and Ag bottom cathodes. Red arrows indicate on which side the respective devices are transparent and emit light. (b) Energy level diagram for all functional layers mentioned in panel a. (c) Color map of the optical transmission of MAM structure with different MoO₃-2 layer thickness. (d) Transmission enhancement of MAM structure with a 25 nm MoO₃-2 layer. Inset in panel d shows transmittance for ITO, M₂₀AM₀, and M₂₀AM₂₅ layers and an EL spectrum of LED. (e) EQE vs current density for LEDs with Ag and ITO cathodes; insets show photographs of the respective working devices. (f) Current density vs driving voltage and luminance vs driving voltage for LEDs with Ag and ITO cathodes.

Figure 3.

XPS spectra of ITO/ETL/CsPbI₃ (black) and Ag/ETL/CsPbI₃ (red) films for (a) Pb 4f, (b) I 3d, and (c) Ag 3d elements. (d) XRD patterns for Ag/ETL/CsPbI₃ (red) and ITO/ETL/CsPbI₃ (black) films.

Figure 4.

(a) Changes of PL QYs (normalized for the initial point) of CsPbI₃ NC films on different substrates (as indicated in the panel) stored in air for 2 days. (b) Changes of EL intensity of CsPbI₃ NC-based LEDs with ITO and Ag bottom layers, in nitrogen atmosphere. (c) PL decays of Ag/CsPbI₃, Ag/ETL/CsPbI₃, and ITO/ETL/CsPbI₃ films. (d) Current density vs voltage curves of the “electron-only” and “hole-only” LEDs, with the respective structures as indicated in the panel.