Dynamics of Photo-Generated Carriers across the Interface between CsPbBr$_3$ Nanocrystals and Au–Ag Nanostructured Film, and Its Control via Ultrathin MgO Interface Layer

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ABSTRACT: The dynamics and control of charge transfer between optoelectronically interesting and size-tunable halide perovskite quantum dots and other juxtaposed functional electronic materials are important issues for the emergent device interest involving such a family of materials in heterostructure configurations. Herein, we have grown bimetallic Au–Ag thin films on glass by pulsed laser deposition at room temperature, which bear nanoparticulate character, and the corresponding optical absorption spectra reveal the expected surface plasmon resonance signature(s). Subsequently, spin-coated CsPbBr$_3$ nanoparticle films onto the bimetallic Au–Ag films exhibit surface-enhanced Raman scattering as well as strong photoluminescence quenching, the latter reflecting highly efficient transfer of photo-generated carriers across the CsPbBr$_3$/Au–Ag interface. Surprisingly, when an ultrathin MgO (insulating) layer of optimum thickness is introduced between the CsPbBr$_3$ and Au–Ag films, the charge transfer is further facilitated with the average lifetime of carriers becoming even shorter. By changing the thickness of the thin MgO layer, the carrier lifetime can in fact be tuned; with the charge transfer getting fully blocked for thick enough MgO layers, as expected. Our study thus throws light on the charge-carrier dynamics in halide perovskites, which is of importance to emergent optoelectronic applications.

INTRODUCTION

Recently, the research on all-inorganic halide perovskites has been attracting great attention because of their size, doping, and surface ligand-based tunability of the attendant properties and thereby their potential usefulness for different photovoltaic and optoelectronic device systems. In particular, the highly photoluminescent CsPbBr$_3$ nanocrystals are being extensively studied because of their various interesting optical properties such as high photoluminescence quantum yields (PLQY), narrow emission spectra, and excellent photo-stability, in addition to the size-tunability. Among the three halide perovskites, namely CsPbX$_3$ (X = I, Br, and Cl), CsPbBr$_3$ is much more stable and exhibits remarkable PLQY (~90%). It is also a direct band gap semiconductor with a gap of ~2.4 eV. Heterostructures comprising semiconductor and metal nanoparticles are also being concurrently explored for plasmonic-electronic devices. The surface plasmonic property of metal nanocrystals is known to facilitate and enhance the absorption and conversion of the photon flux into electrical energy by generating highly energetic or hot electrons. The energy extracted from these hot electrons through their contact with a semiconductor can thus be fruitfully integrated with the functional optoelectronic devices. In the past few years, many efforts have been expended to understand the energy transfer across the perovskite CsPbBr$_3$ nanocrystals and metallic nanoparticles, for example, gold (Au) or silver (Ag), showing enhanced efficiency in device performances.

Both gold and silver nanoparticles have their individual importance when integrated onto a device as they show the localized surface plasmon resonance (LSPR) (collective oscillation of conduction electron induced by incident light) over differing visible wavelength ranges, that is, 520–530 nm (for Au) and 400–420 nm (for Ag). However, compositional dependence for bimetallic nanoparticles (e.g., Au–Ag) exhibits further interesting and tunable electronic, optical, and chemical properties attributed to the bifunctional or synergistic effects. Indeed, there are several reports available in the literature showing that bimetallic nanoparticles containing gold show enhanced catalytic activity and superior sensing. Several reports had shown that surface plasmon resonance frequency can either be blue or red shifted linearly with the increase of Ag or Au content. In addition to the surface plasmon
resonance over the wide spectral range, another advantage of the bimetallic system is the interesting interfacial chemistry of Au−Ag nanoparticles in terms of tuning of the surface-binding affinities at the Au versus Ag sites; thereby influencing the electrical and optical properties. 17 Considering the interesting near-overlap between the surface plasmon peak of Au (which has mostly been used for devices as the metal electrode) and emission peak of monocristalline CsPbBr3, it is of interest to add a small concentration of Ag into Au. The resonance frequency of Ag nanostructures matches well with some of the semiconductors in the ultraviolet region. However, it has been reported as one of the possible ways to modify the range of Ag nanostructure resonance frequency by alloying it with Au nanostructures, which can help to extend the optical light absorption range, hence strongly influencing the light absorption capacity of the embedded perovskite materials. Also, visible light-induced intraband excitations can generate high-energy hot electrons and holes in Ag plasmonic nanostructures, whereas interband excitations in Au plasmonic nanostructures produce low-energy hot electrons. 21 Therefore, it is important to explore the possible tuning of the optoelectronic functionality of the layered composite of perovskite CsPbBr3 with bimetallic Au−Ag nanostructures in the device worthy nanoparticulate film format.

Another aspect of academic and technical interest is the interesting role played by ultrathin insulating layers in multilayer heterostructure device systems. When an ultrathin insulating dielectric layer is introduced between the different functional layers, some unusual phenomena have been noted such as the spin reversal effect. 22 For the current case of Au−Ag−MgO, MgO can serve as one of the excellent barrier layers for high-temperature growth,27,28 and promotes lateral growth that results in the smooth surface morphology and layer-by-layer growth.27,28 Recently, it has also been shown that when ultrathin MgO is introduced on the metal thin films, the work function of metal films can be tuned, which affects the quantum efficiency and hence the optoelectronic properties. 23,24,25 Moreover, in thin film growth, an ultrathin MgO layer can also facilitate the initial nucleation and promotes lateral growth that results in the smooth surface morphology and layer-by-layer growth. 27,28 All these studies suggest that understanding and control of the interfacial charge-transfer process of halide perovskite integrated with the bimetallic plasmonic Au−Ag nanostructure and an insulating layer in-between are extremely important for future high-performance optoelectronic devices, for example, halide perovskite-based solar cells and light-emitting diodes.

Based on the abovementioned considerations, in this work, we first investigated the effect of the proximity of bimetallic Au−Ag nanostructures on the optoelectronic properties of monocristalline CsPbBr3. Then, we examined the effects of adding ultrathin insulating MgO buffer layers in-between of CsPbBr3 nanocrystals and bimetallic Au−Ag nanostructured thin films. Remarkably, introduction of an ultrathin MgO (insulating) layer of optimum thickness facilitated and enhanced the efficiency of transfer of the photo-generated carriers with the average lifetime of carriers becoming much shorter. With change in the thickness of the MgO layer, the carrier lifetime could be easily tuned, and the charge transfer was fully blocked for thick enough MgO layers, as expected.

## RESULTS AND DISCUSSION

In order to grow metallic Au−Ag thin films, we used the pulsed laser deposition (PLD) method, wherein a pulsed UV laser (a KrF laser with the wavelength 248 nm and pulsed width of 20 ns) was employed to ablate the target. When such a laser pulse hits the target surface, a high-energy plume containing ions, molecule, and radicals emanates from the target surface, impinges onto the substrate surface, and condenses into the solid-state film form within a few microseconds. 23 Although it is a nonequilibrium ablation process, it can enable growth of atomically and stoichiometrically controlled high-quality thin films. Herein, by using high purity individual Au and Ag metal targets, we grew Au−Ag thin films first with the deposition of Au and then Ag. After deposition, films thickness was measured by using the atomic force microscopy (AFM) (Figure S1). The thickness equivalent of Au and Ag was 9:1, as also confirmed by scanning electron microscopy (Figure S2).

The optical images of a typical glass substrate and the same with a 10 nm Au−Ag film are shown in the Figure 1a reflecting the change in transparency. X-ray diffraction (XRD) pattern is shown in Figure 1b, and it shows the (111), (200), (220), and (311) Bragg peaks of Au (or Ag which almost overlap) throughout the 2θ scan range of 30°–80°. Indeed, the lattice constants of Au and Ag being almost the same, that is, 4.078 Å (for Au) and 4.085 Å (for Ag), the XRD of Au and Ag are indistinguishable within the resolution available as they almost merge. The AFM reveals island-type growth with surface roughness of 1 nm (inset of Figure 1b). For transmission electron microscopy (TEM) analysis, we deposited the film on carbon-coated Cu-grid, and the corresponding image (Figure 1c) reveals the nanoparticulate nature of the films. One can
clearly see the line profile, with the distance of 0.24 nm, corresponding to the d-spacing along the (111) diffraction plane of the face-centered cube of Au or Ag. Moreover, the elemental mapping (Figure 1d) shows that both the Au and Ag particles are uniformly distributed throughout the nanostructured film. Resistivity of the Au–Ag nanostructured film was found to be ~10−6 Ω m at room temperature (Figure S3).

The UV–vis absorption spectrum of the Au–Ag nanostructured film is shown in Figure 2. For comparison, we have also plotted the spectra for pure Au and Ag films. Because of the ultrathin nanostructured characteristics, both Au and Ag metallic films show the LSPR peak at 492 nm (for Au) and 317 nm (for Ag), respectively. In comparison, the bimetallic Au–Ag nanostructured film shows a much broader LSPR signature at 468 nm, which is blue (red) shifted with respect to the Au (Ag), consistent with the numerical calculations based on the Drude model and quasi-static theory by Zhu.

One can notice that the bimetallic nanostructure film shows only one surface plasmon resonance peak even though it consists of two metals (Au and Ag). This clearly suggests that Au and Ag nanoparticles are distributed homogeneously. This is a consequence of the amplification of light-induced processes because of the localization of atoms and/or molecules at the surface, giving rise to the surface-enhanced Raman scattering (SERS). Moreover, the surface plasmon peak position also depends on the structure as well as the composition of the bimetallic nanoparticles. Therefore, it is very interesting to grow these kind of bimetallic nanostructures for tunable optoelectronic functionalities.

As mentioned earlier, the perovskite CsPbBr3 nanocrystal photoluminescence (PL) could be significantly tuned by localized surface plasmon of Au as the surface plasmon peak of Au (~492 nm) almost overlaps with the emission peak of CsPbBr3 nanocrystals (~515 nm). In contrast, Ag shows the strong surface plasmon peak at a much lower wavelength of ~317 nm. In order to check how the PL properties of CsPbBr3 are influenced by the bimetallic Au–Ag nanostructured thin films having broad absorption with a surface plasmon peak at ~468 nm, we spin-coated the colloidal solution of CsPbBr3 nanocrystals onto the bimetallic Au–Ag film and tested the PL properties of the heterostructure. The TEM image of the CsPbBr3 nanocrystals is shown in Figure 3a. It shows the expected cubic shape nanocrystals having sizes of ~11 nm. These nanocrystals are slightly larger than the corresponding Bohr excitonic diameter of ~7 nm, exhibiting a weak quantum confinement effect on charge carriers. It has been reported that in order to exhibit high transition probability for PL, weak confinement of charge carrier is sufficient. The XRD of the pure CsPbBr3 nanocrystals and spin-coated CsPbBr3/Au–Ag heterostructures are shown in Figure 3b. These structures show oriented (110) and (220) peaks of CsPbBr3 along with the (111) Bragg peak of Au–Ag. Also, the cross-sectional field emission scanning electron microscopy (FESEM) image shows the formation of individual Au–Ag and CsPbBr3 layers (Figure S4a).

To observe the effect of localized surface plasmons, we performed Raman spectroscopy of the CsPbBr3/Au–Ag films. We noted enhancement in the Raman intensity when nanoparticles of bimetallic Au–Ag thin films were used as a platform for the deposition of CsPbBr3 nanocrystals with respect to the pristine CsPbBr3 on glass (Figure 3c). It is a consequence of the plasmonic resonance of the bimetallic Au–Ag films, providing the intense optical frequency field responsible for the electromagnetic contribution in the SERS. Because of highly metallic characteristics and formation of large number of localized plasmons at the junction between Au–Ag and CsPbBr3, the frequency field increases giving rise to the SERS with a significant increase in the Raman intensity.

As shown in Figure 4a, we compare the PL intensity of the heterostructure between the pristine CsPbBr3 quantum dot (QD) film on glass and CsPbBr3 QD film on Au–Ag-deposited glass. The intensity in the latter case is seen to be significantly reduced with respect to the case of pristine CsPbBr3, confirming the direct influence of the Au–Ag nanostructure on the excited-state properties of nanocrystalline CsPbBr3, most possibly in the form of charge transfer across the interface. It is important to note here that the absolute PL intensity is a tricky quality factor to analyze because it depends on the net absorbance in the photoactive material and the scattering effects. One can resort to normalization vis-à-vis the absorbance at the excitation wavelength used (as performed in our case) but that too has limitations to the degree of

Figure 3. (a) TEM image shows the formation of ~11 nm cubic shape CsPbBr3 nanocrystals. The line width of ~0.32 nm corresponds to the d-spacing of the (200) diffraction plane. (b) XRD patterns of the CsPbBr3 and CsPbBr3/Au–Ag film showing the oriented peaks. (c) Surface-enhanced Raman spectra of the CsPbBr3/Au–Ag film is shown.

Figure 2. UV–vis absorption spectrum of bimetallic Au–Ag nanostructured thin film showing the characteristic surface plasmonic peak arising from the oscillation of free electrons. Pure Au and Ag film absorption spectra are shown for the comparison.

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correctness, especially in the case of complex heterostructures involving nanosystems such as the ones we have addressed in this study. Moreover, the argument that PL intensity increase (decrease) must necessarily mean reduced (enhanced) charge transfer can only be justified if the full change in PL intensity because of interface formation is entirely assigned to charge transfer. At a real interface involving functional molecules, the situation is more complex with interface states/defects and their role in passivation, leading to enhanced PL of the active material itself.34 This is particularly important in cases such as CsPbBr3 QDs wherein the excitonic recombination is mainly known to be governed by surface states and thus the formation of interfaces based thereupon can clean or pollute these states.35

More interesting and perhaps a more direct signature of charge transfer can be garnered from the results of time-resolved PL (TRPL) studies. As shown in Figure 4b, we can clearly see a significant change in the TRPL between these two cases of interest, which strongly suggests rapid bleaching of PL by charge transfer across the interface between CsPbBr3 QDs and the bimetallic Au–Ag nanostructure. We will discuss this further when we compare the TRPL results for all the cases of interest. Another interesting change between the two cases is the blue shift (~2 nm) in the PL of CsPbBr3 QDs while in proximity of the bimetallic Au–Ag nanostructure. This is an electronic consequence of the interaction between semiconductor and metal nanoparticles caused by carrier transfer seeking a new equilibrium (the same phenomenon that conductor and metal nanoparticles caused by carrier transfer. At a real interface involving functional molecules, the electronic consequence of the interaction between semi-proximity of the bimetallic Au–Ag nanoparticles also in the perovskite, that is, smaller particles (~1–2 nm) have smaller influence and vice versa.11 Considering the Au–Ag nanoparticles have sizes of ~40–50 nm (as observed through scanning electron microscopy), one would expect a very strong influence on the excited-state properties of CsPbBr3 because of the larger plasmonic particles.

We then examined the consequences of introducing a thin insulating MgO buffer layer at the interface between CsPbBr3 and bimetallic Au–Ag thin films for the PL, systematically. Thus, we deposited MgO onto the already grown Au–Ag nanostructured thin film and then spin-coated the CsPbBr3 colloidal solutions. The individual layers of Au–Ag, MgO, and CsPbBr3 are shown in Figure S4b (for imaging clarity, the MgO layer was grown a bit thicker in this case). As shown in Figures 5a and S5, we present the changes in the normalized (w.r.t. excitation wavelength absorbance) PL intensity for the CsPbBr3/MgO/Au–Ag nanostructured films with varying thicknesses of the thin MgO layer. It can be seen that for the case of a 0.5 nm MgO separation layer, the PL intensity is further reduced, and the small blue shift mentioned earlier is also suppressed because now a new interface is involved. As the separator layer thickness is increased to 1 and 5 nm, the normalized PL intensity partially recovers, and the blue shift is noted once again. For a much thicker (10 nm) MgO layer, the PL intensity recovers further with reduced blue shift.

The TRPL study was also performed to better understand the charge-transfer dynamics in CsPbBr3/Au–Ag and CsPbBr3/MgO/Au–Ag thin films, as shown in Figures 5b and S5. The biexponentially fitted fast and slow decay components (τ1) ~3.1 ns (57.6%) and (τ2) ~12.7 ns (42.3%) for CsPbBr3 correspond to the bound and free exciton recombinations, respectively.36 For the case of CsPbBr3/Au–Ag thin film, lifetimes (τ1) ~2.2 ns (65.70%) and (τ2) ~12.3 ns (34.20%) were obtained which are considerably different, as compared to the only CsPbBr3 case. Specifically, the fast component contribution increased from 57.67 to 65.70%, and the lifetime is reduced considerably (from 3.1 to 2.2 ns). This further suggests that the photo-generated charge carriers promptly cross the interface between the CsPbBr3 and Au–Ag nanostructures. Notably, these transferred charges lead to

Figure 4. (a,b) Steady-state PL spectra and TRPL lifetime curve showing the quenching as well as faster charge transport for the CsPbBr3/Au–Ag with respect to the pure CsPbBr3.

Figure 5. (a,b) Steady-state PL spectra and TRPL lifetime curve of the CsPbBr3/Au–Ag film with sandwiched insulating MgO thin film having different thicknesses.
nonradiative decay that does not contribute to PL. The slower lifetime value is not changed as much, as expected; however, the relative percentage for the fast decay in this case is higher in comparison to that for the pristine CsPbBr₃ thin film. This contribution is identified with the nonradiative relaxation of hot electrons (generation in plasmonic nanostructures during interband or intraband excitations) because of electron–electron and electron–phonon collision, dissipating energy to the lattice in the form of heat.⁵⁷

One would normally expect the charge transfer to be inhibited by the interposed wide-band gap insulating MgO resulting in a gain in the PL intensity and carrier lifetime, but we observed a remarkably interesting phenomenon of rapid time relaxation of PL for the cases of ultrathin 0.5 (as shown in Figure S5) or 1 nm MgO separation layer between the CsPbBr₃ QD film and Au–Ag. Interestingly, PL relaxation for a 1 nm case was found to be much faster than that for a 0.5 nm MgO case or even for the case of CsPbBr₃ on Au–Ag without MgO. Concurrently, the PL intensity for a 1 nm MgO case was higher than that for a 0.5 nm MgO sample.

The TRPL decay profiles of CsPbBr₃/Au–Ag nanostructured films with varying thicknesses of the MgO layer are compared in Figures S5b and S5c; the comparison clearly shows a significantly faster PL intensity decay for the CsPbBr₃/MgO/Au–Ag heterostructures with an ultrathin MgO layer, as compared to the CsPbBr₃ case and the CsPbBr₃/Au–Ag case. The data with bi-exponential fitting for different cases of interest are summarized in Tables 1 and S1.

### Table 1. Lifetime of Carriers (via Biexponential Decay Fitting) across the CsPbBr₃/Au–Ag Interface for Varying MgO Layer Thicknesses

| Sample | τ₁ (ns) | α₁ | τ₂ (ns) | α₂ |
|--------|---------|----|---------|----|
| CsPbBr₃ | 3.1     | 57.67 | 12.7 | 42.33 |
| CsPbBr₃/Au–Ag | 2.2     | 65.70 | 12.3 | 34.20 |
| CsPbBr₃/MgO (1 nm)/Au–Ag | 1.6     | 62.00 | 6.7 | 38.00 |
| CsPbBr₃/MgO (10 nm)/Au–Ag | 3.3     | 53.06 | 11.0 | 46.94 |

In the case of CsPbBr₃/MgO (0.5 nm)/Au–Ag, the fast component (τ₁) 2.1 ns (51.34%) and slow component (τ₂) 10.1 ns (48.66%), show a clear reduction in the decay time. The case of 1 nm MgO interposed layer clearly appears to be the most interesting one with a significant impact on the carrier relaxation process (see Table 1). In the CsPbBr₃/MgO (1 nm)/Au–Ag case, the lifetimes are (τ₁) 1.6 ns (62%) and (τ₂) 6.7 ns (38%) showing considerable reduction in relaxation times, as compared to the CsPbBr₃/Au–Ag case. The contribution of the fast component is quite significant in this case as well. Notably, the significant decay in lifetime and steady-state luminescence quenching could also be attributed to the involvement of plasmon resonance energy transfer generated from dipole–dipole relaxation.⁵⁸ It is possible that the nominally 0.5 nm thick MgO insulating layer for the CsPbBr₃/MgO (0.5 nm)/Au–Ag case does not have a full uniform coverage and renders a result that is between that for the CsPbBr₃/Au–Ag and CsPbBr₃/MgO (1 nm)/Au–Ag case. However, for thicker MgO insulating layers (which progressively isolate the CsPbBr₃ QDs from the Au–Ag layer), the lifetimes return to the values of the only CsPbBr₃ case, as expected. In addition, it is useful to state here that the calculated optical density for pure CsPbBr₃ is 1.036, while the optical densities for CsPbBr₃/Au–Ag and CsPbBr₃/MgO (1 nm)/Au–Ag films have almost comparable values, that is, 0.927 and 1.035, respectively. Thus, the luminescent material is getting excited equally in all the cases keeping all the parameters same. We also show the band alignment, as shown in Figure 6, for its relevance to this discussion.

Several very interesting papers published in the literature have addressed the effects and consequences of the proximity of a dielectric layer with a metal surface. In many of these, MgO is used because of some unique effects that it exhibits. Giordano and Pacchioni suggested that changes in work function and appearance of mid-gap states are responsible for some surprising behaviors of such interface systems.⁵⁹ They have also shown that ultrathin (<1 nm) films can in fact lead to unusual properties, as compared to thicker films, along the line seen in the present work. Hollerer et al. have performed detailed comparative experimental and theoretical studies of pentacene adsorbed on Ag(001) with and without an ultrathin MgO interlayer.⁶⁰ It was found that the dielectric layer is not simply a passive layer for decoupling purposes but an active participant in the phenomena via influence on orbital energy level alignment and charge transfer at the interface, the latter being the issue addressed in this work. Indeed, their work further suggests that the ultrathin dielectric layer can reduce the electron injection barrier by work function reduction. Vaida and Bernhardt have also examined the photo-dissociation dynamics of sub-monolayer CH₃Br on Mo(100) with or without an ultrathin MgO layer and shown that energetic lowering of excited electronic states of the adsorbate and change in the adsorption geometry can have interesting implications.⁶¹ In the specific cases of CsPbBr₃ and CsPbCl₃ nanocrystals, the role of surface states, defects, and their passivation in controlling the recombination dynamics via their carrier population and transfer has also been highlighted in various studies.⁶²,⁶³ Pacchioni and Freund in their extensive review have also addressed the issue of carrier transfer in ultrathin films with specific focus on the binary MgO case,⁶⁴ which clearly distinguishes itself from other reducible functional transition metal oxides which can change their oxidation state and trap the carrier. Thus, the interface conditions with the (001) planes of cubic CsPbBr₃ crystals being stationed on Au–Ag bimetallic nanocrystals versus being anchored on ultrathin MgO layers are entirely different in the context of charge transfer in terms of proximity effects. Thus, the reduction of the electron injection barrier caused by the reduction in the work function and the possible presence of mid-gap states facilitating charge transfer could be responsible for the notable changes (especially reduction of lifetime) observed for an optimum 1 nm thick MgO separator layer. In our case of nanostructured interfaces, one could also envision the changes in the surface plasmon frequencies because of...
dielectric proximity also contributing to the changes in charge transfer.

**CONCLUSIONS**

In summary, we have investigated the optoelectronic properties of nanocrystalline CsPbBr₃ halide perovskite integrated with bimetallic Au−Ag nanostructured thin films, exhibiting a PL quenching phenomenon; a consequence of the transfer of photo-generated carriers across the interface. Remarkably, an ultrathin 1 nm insulating MgO layer placed between CsPbBr₃ and Au−Ag films shows significantly enhanced charge-transfer efficiency, as compared to the case without such a layer; while thicker films gradually arrest the transfer because of enhanced decoupling of the CsPbBr₃ QD layer and the Au−Ag layer. These results have a bearing on the design of multilayered optoelectronic devices based on halide perovskite nanocrystals.

**EXPERIMENTAL SECTION**

**Thin Film Growth.** Both Au−Ag and MgO films were grown on glass (cover slip size: 1.8 cm × 1.8 cm) via PLD (a KrF laser of the wavelength 248 nm and pulse width of 20 ns). For the growth, high purity Au and Ag metal targets were used. Films were grown under high vacuum and at room temperature. First, Au films were grown and then subsequently Ag were deposited. The composition was controlled by fixing the number of laser shots. The repetition rate was 5 Hz, while keeping the target to the substrate distance of 40 mm. Then, we have grown MgO films at 400 °C and in 100 mTorr oxygen atmosphere by keeping the repetition rate 5 Hz. We deposited various thickness samples by using different numbers of laser shots for the MgO growth. The CsPbBr₃ solution (100 μL) was spin-coated onto the Au−Ag and Au−Ag/MgO thin films by using POLOS spin-coating instrument with 2000 rpm for 60 s.

**Synthesis of CsPbBr₃ Nanocrystals.** Colloidal nanocrystals of CsPbBr₃ were grown following the procedure given in ref 7. A magnetically stirred mixture of PbBr₂ (0.188 mmol) with 5 mL dried 1-octadecene (ODE) was degassed (under alternate vacuum and nitrogen) at 120 °C. At the same temperature, dried oleic acid and oleylamine, each 0.5 mL, was added to the mixture. After ca. 30 min, PbBr₂ is dissolved in ODE, and we increased the temperature to 190 °C. Then, we swiftly injected the Cs-oleate (0.1 M, 0.4 mL) solution in ODE, and we increased the temperature to 190 °C. The mixture became greenish, and we stopped the reaction by dipping the reaction flask into an ice bath. The synthesized CsPbBr₃ nanocrystals were precipitated by adding 15 mL tert-butanol at room temperature and then centrifuged at 7000 rpm. The nanocrystals were finally washed twice with methyl acetate and redispersed in 2 mL octane for further studies.

**Structural Characterizations (XRD, AFM, TEM, Raman, and FESEM).** For XRD, a Bruker D8-Advance X-ray diffractometer (Germany) with a Cu Kα X-ray source (λ = 1.5406 Å) has been used with an operating voltage of 35 kV and current of 30 mA. TEM images were taken with a JEOL JEM-220FS series 200 kV system transmission electron microscope. For TEM, the wet pellet of the nanocrystals was dispersed in 5 mL of toluene, and the solution was placed in the carbon-coated Cu TEM grid and dried before placing it into the TEM. We used Nanosurf (Switzerland) AFM for the surface topography analysis and measuring the thickness of the films. Raman spectra of the films were recorded with a 2.33 eV (~532 nm) excitation energy laser. The cross-sectional morphologies were scanned by FESEM (JEM-2100F, JEOL, Japan). The energy-dispersive analysis of X-rays (EDAX) was also performed using the same instrument.

**Optical Characterizations (Absorbance and PL).** UV−visible spectra were recorded using a Thermo Scientific (Evolution 300) UV−vis spectrometer. Steady-state PL and TRPL were measured using FLS 980 (Edinburgh Instruments). For PL, we used a xenon laser with excitation of 450 nm. For TRPL, we used the diode laser with the wavelength of 405 ± 10 nm and the maximum average power of 5 mW.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03817.

Morphological, electrical, and optical characterizations of films (PDF)

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**Notes**

The authors declare no competing financial interest.

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