1. Introduction

The growing demand for renewable energy has brought solar cells to the forefront as a potential energy harvester. Consequently, organic–inorganic metal halide perovskite solar cells have garnered profound research interest in recent years as next-generation photovoltaics.\(^1\) This importance stems largely from their exceptional charge carrier mobilities, and optical and electronic properties that are tunable by varying the chemical composition.\(^2,3\) Recently, perovskite-based solar cells have demonstrated an impressive power conversion efficiency (PCE) of over 20%.\(^4\) In most of the practical applications of solar cells, besides the importance of short-circuit current density, high open-circuit voltage \(V_{oc}\) is an indispensable parameter to attain both high power conversion efficiency with reduced series resistance losses and to drive electrochemical reactions including water-splitting reactions and \(\text{CO}_2\) reduction.\(^5,6\)

In principle, a high open-circuit voltage in a perovskite solar cell can be attained by aligning the energy levels of absorber and charge extraction layers.\(^7\) Despite having enticing benefit of higher bandgap for pure bromide-based perovskite material
which indeed can also be used as a top cell in tandem solar cells,[8] much of the research mainly focused on pure iodide (CH₃NH₃PbI₃), mixed halide (CH₃NH₃PbIₓBr₁₋ₓ) or double-mixed ((CH₃NH₃)₂PbI₃(CH₃NH₃PbBr₃)ₓ perovskites.[4] Nevertheless, promising studies on efficient methylammonium lead bromide (CH₃NH₃PbBr₃)-based device architecture showing enhanced photovoltaics in comparison to pure iodide-based perovskite have been documented. Kojima et al. reported on employing CH₃NH₃PbBr₃ as visible-light sensitizers in photoelectrochemical cells exhibiting a promising photovoltage of 0.96 V with a power conversion efficiency of 3.1%.[9] Later on, Edri et al. described a high Voc of 1.3 V based on aluminia\CH₃NH₃PbBr₃\N,N′-dialkyl perylenediimide (PDI) solar cell structure, however the efficiency of the devices was quite low (< 1%).[10] Recently, by controlling the crystallization process of CH₃NH₃PbBr₃ as well as by tailoring the highest occupied molecular orbital (HOMO) levels of different hole-transporting materials (HTMs), a Voc of 1.51 V has been reported.[11] So far, most of the studies on bromide perovskites are devoted to CH₃NH₃PbBr₃, however, the focus of this work constitutes formamidinium lead bromide (CH₃NH₃PbBr₃ = FAPbBr₃) perovskite which has been studied scantily. Earlier, Hanusch et al. described the fabrication of planar heterojunction FAPbBr₃ perovskite solar cells with efficiency of over 6%.[12] however, the device exhibited severe hysteresis which leads to an overestimation of power conversion efficiency. Mostly the presence of mesoporous TiO₂ scaffold has proven to be advantageous in reducing the scan speed dependent hysteresis observed in current–voltage (J–V) curves in perovskite solar cells.[13,14] Tuning the growth of perovskite structures has been one of the critical parameters to fabricate high-efficiency solar cells. To that end, we investigated the role of solvent on the growth and morphology of FAPbBr₃ perovskite films, which eventually led to the enhancement in the photovoltage to a remarkable extent. We fabricated FAPbBr₃ films employing the sequential deposition method involving a mixture of solvents, N,N-dimethylformamide and dimethyl sulfoxide(DMF+DMSO) for the PbBr₂ precursor solution. Employing spiro-OMeTAD as a hole-transporting material led us to fabricate FAPbBr₃ perovskite devices with a Jsc of 6.8 mA cm⁻², FF of 72%, and Voc of 1.42 V resulting in an overall efficiency of 7.0%. It is to be noted that these devices exhibited negligible hysteresis. The impact of the solvent on structural, morphological, and various photophysical properties which dictate the photovoltaic performance of a device was explored by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV–visible absorption, low temperature photoluminescence (PL), and charge carrier lifetime studies.

Additionally, amplified spontaneous emission (ASE) was recorded from the FAPbBr₃ perovskite films. Recently, there has been a report in which formamidinium lead bromide perovskite nanoparticles were incorporated into light-emitting electrochemical cells.[15] In the literature various studies have demonstrated the enormous potential of perovskite materials as optical gain mediums even with a cavity-free configuration.[16,17] The low nonradiative recombination rate, long diffusion length, and high mobility of charge carriers reported for perovskites even with high defect trap densities, are key factors for their unprecedented progress in photovoltaics.[18–20] In addition to slow Auger recombination, the various possibilities of fabricating them in different cavity configurations make them suitable for an efficient semiconductor laser.[21–23] In this work, a sharp transition from spontaneous emission (SE) to ASE at a pump fluence of 190 µJ cm⁻² per pulse was observed in FAPbBr₃ perovskite films which corresponds to an ASE threshold carrier density of ≈2.3 × 10¹⁸ cm⁻³. Although ASE has been reported for both CH₃NH₃PbI₃ and CH₃NH₃PbBr₃ perovskites in different resonating and cavity-free configurations as well as in random networks of nanocrystals,[16,17,21–23] to the best of our knowledge, there has been no report till date demonstrating the light gain applications of such FAPbBr₃ perovskite films.

2. Results and Discussion

Two different FAPbBr₃ perovskite films were deposited using the sequential deposition approach. Typically, a solution of PbBr₂ (DMF) or PbBr₂ (DMF+DMSO) was spin casted onto a mesoporous TiO₂ scaffold. Subsequently the resulting films were converted into FAPbBr₃ perovskite films by dipping into isopropanol solution of formamidinium bromide (CH₃NH₃Br), which were labeled as FA(1) (obtained from PbBr₂ (DMF)) and FA(2) (obtained from PbBr₂ (DMF+DMSO)). (See the Experimental Section for more details.)

2.1. Structural and Morphological Characterization

To evaluate the crystallinity of FA(1) and FA(2) perovskite films, X-ray diffraction was performed at room temperature. The XRD patterns (Figure S1, Supporting Information) obtained from the films could be indexed to the cubic phase of FAPbBr₃ with a space group Pm–3m, which is consistent with previous reports.[12,15] The morphology of lead bromide and FAPbBr₃ films was probed by FESEM. From SEM analysis, it is evident that coverage of the lead bromide films obtained from PbBr₂ (DMF) (Figure 1a) solution is relatively poor whereas the deposition of PbBr₂ (DMF+DMSO) solution led to the formation of a uniform lead bromide film (Figure 1b). Furthermore, top view SEM micrograph of FA(1) perovskite sample reveals the formation of an inhomogeneous film composed of aggregated FAPbBr₃ structures (Figure 1c). On the contrary, extremely uniform and continuous FAPbBr₃ films with full surface coverage were obtained in case of FA(2), as shown in Figure 1d. From a marked difference in the surface morphology of lead bromide and FAPbBr₃ films for FA(1) and FA(2) samples, we establish that the nature of the solvent employed for PbBr₂ precursor solution can considerably improve the surface coverage of the films, which ostensibly could be beneficial for the fabrication of efficient devices.[13] The device fabrication was completed by spin coating spiro-OMeTAD as the hole-transporting material on FAPbBr₃ perovskite layer, followed by thermal evaporation of a 70 nm thick gold layer as a back contact. The cross-section SEM micrograph of FA(1) (Figure 1e) shows the formation of a nonuniform FAPbBr₃ film of ≈500 nm thickness (including mesoporous TiO₂).
pronounce the amorphous nature of lead iodide films. Using DMSO–lead iodide adduct, the fabrication of high-efficiency solar cells has been reported recently. To understand the role of DMSO further, we recorded XRD patterns of FA(1) and FA(2) lead bromide films. Variation in the crystal structure of lead bromide films deposited from a single and a stoichiometric mixture of DMF+DMSO solvent (Figure S4, Supporting Information) was marginal which is in contrast to what has been observed in lead iodide films.

2.2. Photovoltaic Properties of Formamidinium Perovskite Devices

Tailoring the growth and morphology of perovskite layer is one of the critical factors that led to the evolution of high-efficiency perovskite solar cells. Herein, we investigated the effect of morphology of FAPbBr₃ films on the performance of the resulting devices. The current–voltage curves of the FA(1) and FA(2) bromide perovskite devices are shown in Figure 2 and the extracted photovoltaic parameters are summarized in Table 1. Under illumination of 100 mW cm⁻², the device based on FA(1) film (FAPbBr₃ film involving PbBr₂ (DMF) precursor solution) exhibits a high short-circuit current density \( J_{sc} \) of 7.1 mA cm⁻², a modest open-circuit voltage \( V_{oc} \) of 1.14 V, and a fill factor (FF) of 0.67, resulting in an overall power conversion efficiency (\( \eta \)) of 5.4% (Figure 2a). By contrast, FA(2) device exhibits similar short-circuit current density \( J_{sc} \) of 6.8 mA cm⁻², a record \( V_{oc} \) for formamidinium perovskite of 1.42 V, and a FF of 0.72, resulting in an overall conversion efficiency (\( \eta \)) of 7.0% (Figure 2b). Ostensibly, a higher \( J_{sc} \) value of 7.1 mA cm⁻² obtained from FA(1) device could be due to the formation of thicker FAPbBr₃ films as evident from cross-sectional SEM analysis (Figure 1e). By changing the solvent from DMF to a stoichiometric mixture of DMF+DMSO solvents for the PbBr₂ precursor solution, \( V_{oc} \) increases significantly from 1.14 to 1.42 V which demonstrates that the morphology of the film has a considerable impact on the photovoltage.

2.2.1. Insight into the Origin of High \( V_{oc} \)

The \( V_{oc} > 1.4 \) V for FA(2) devices is extraordinarily high considering the contact materials FTO/TiO₂ and spiro-OMeTAD. Assuming that the work function of the FTO/TiO₂ is \( \approx -4.0 \) to \( -4.2 \) eV and the HOMO in the doped spiro-OMeTAD at \( -5.4 \) eV and, thus, the work function close but smaller than this value, \( V_{oc} \) is larger than the built-in potential. Therefore, the energetics of the contact materials do not merely define the \( V_{oc} \) as commonly reported in the literature. Such a high \( V_{oc} \) is
Table 1. Summarized photovoltaic parameters derived from current–

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
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<tbody>
<tr>
<td>FA(1)</td>
<td>7.1</td>
<td>1.14</td>
<td>67</td>
<td>5.4</td>
</tr>
<tr>
<td>FA(2)</td>
<td>6.8</td>
<td>1.42</td>
<td>72</td>
<td>7.0</td>
</tr>
</tbody>
</table>

molecular orbital (LUMO) of spiro-OMeTAD referred to the energy levels of FAPbBr$_3$ and might be enhanced by dipoles formed at the interfaces. A further indication for the high selectivity is given by the fact that the $J$–$V$ curves for FA(2) devices (Figure 2) under illumination and in the dark do not show a pronounced point of intersection.

Biasing the device in forward and collecting the emitted photon flux of electrons and holes that radiatively recombine in the FAPbBr$_3$, we measure an electroluminescence external quantum efficiency (EQE) of $\approx 10^{-5} \ldots 10^{-7}$ for currents of 5–10 mA cm$^{-2}$. Considering the photovoltaic EQE onset (Figure S3, Supporting Information), we expect a photovoltage of $V_{oc}$, nonrad. loss $= 2.0 - 0.5 = 1.5$ V.[33] This rough estimation is in decent agreement with measured values of $V_{oc}$ close to 1.45 V for this device.

Such a significant improvement in photovoltage is further investigated by impedance spectroscopy (IS). The measurements based on impedance spectroscopy revealed a clear difference in the resistive response of FA(1) and FA(2) devices. With increasing forward voltage, both the resistances (determined at higher as well as lower frequency range) dropped faster for FA(1) device (Figure S6, Supporting Information). Relatively faster nonradiative recombination can explain a lower open-circuit voltage obtained from FA(1) devices.[31,34,35]

The reproducibility of our results is ascertainment by depicting the photovoltaic efficiency derived from $J$–$V$ measurements for a batch of 20 devices (Figure S7, Supporting Information). Around 80% of the devices exhibited a photovoltage $> 1.4$ V under illumination of 100 mW cm$^{-2}$, further confirming excellent reproducibility of our results. It is worth mentioning that the photovoltaic of FAPbBr$_3$ devices remained remarkably stable upon prolonged storage under ambient conditions for more than 3 months (Figure S8, Supporting Information).

Due to the accumulation and migration of ions at various interfaces and within the perovskite solar cells, scan speed dependent hysteresis is observed in current–voltage curves.[36,37] Arguably, hysteresis creates discrepancy in estimating the real photovoltaic parameters obtained from a $J$–$V$ curve.[38]
Comparative analysis of photovoltaic studies of perovskite film formation.

Figure 6 shows the evolution of emission spectra with increasing pump fluence of 450 nm laser excitation pulses. At low fluence, emission spectrum corresponding to SE centered at ~550 nm was observed. However, over pump fluence threshold, SE is accompanied with the appearance of a sharp peak (transition to ASE) on the lower wavelength side of SE centered at ~550 nm.

2.3.3. Amplified Spontaneous Emission

Amplified spontaneous emission measurements were carried out on FA(1) and FA(2) films after pumping them with 70 ps laser pulses with tunable wavelengths. ASE was fluently observed in both samples with wide range of pumping wavelengths (430–530 nm). Figure 6 shows the evolution of emission spectra with increasing pump fluence of 450 nm laser excitation pulses. At low fluence, emission spectrum corresponding to SE centered at ~550 nm was observed. However, over pump fluence threshold, SE is accompanied with the appearance of a sharp peak (transition to ASE) on the lower wavelength side of SE centered at ~550 nm.
energy side of the broad bands, centered at 557 and 560 nm for FA(1) and FA(2) samples, respectively.

FA(1) sample displays a slower ASE growth with increasing pump fluence, which makes it more difficult to define the threshold of ASE precisely. Using the two-segment method, ASE threshold of \( \approx 615 \ \mu \text{J cm}^{-2} \) was estimated, which corresponds to a threshold carrier density of \( \approx 7.5 \times 10^{18} \ \text{cm}^{-3} \). On the other hand, FA(2) sample showed a sharp transition from SE to ASE at a pump fluence of 190 \( \mu \text{J cm}^{-2} \) per pulse which corresponds to an ASE threshold carrier density of \( \approx 2.3 \times 10^{18} \ \text{cm}^{-3} \) (Figure 6c). The absorbance spectrum, thickness and porosity of mp–TiO2 layer were taken into account for estimating threshold carrier densities. The carrier density values are in agreement with the values reported for MAPbI3 perovskites, indicating that organic cation contributes marginally to the density of states in organic–inorganic lead halide perovskites.

Furthermore FA(2) sample shows a higher quantum efficiency (Figure 6c) (as can be deduced from the sharp slope in the linear region), whereas FA(1) sample suffers from a...
reduced quantum efficiency, faster ASE saturation and lesser quantum yield. Such a strong contrast between the two samples clearly illustrates the importance of experimental conditions employed for the synthesis of FAPbBr3 perovskite to achieve desired electro-optical properties. This is not trivial as the realization of high performance in solar cells can be reflected in efficient ASE characteristics as well. Comparatively, FA(2) sample displayed better performance most likely because of lower nonradiative recombination rates which are also evident from PL studies. Therefore, we contend that growth and morphology of the perovskite structures considerably influence the nature and type of defects/traps which could affect their optical gain applications.

3. Conclusion

In summary, our work demonstrated the critical role of solvent in controlling the growth of FAPbBr3 perovskite structures. Morphological studies revealed that the surface coverage of the perovskite films remarkably improves when PbBr2 films are deposited from a stoichiometric mixture of DMF and DMSO solvents. To account for these findings, we surmise that besides the enhancement in solubility, employing a mixture of solvents slows down the growth of the lead halide structures during spin coating thus yielding a uniform film with complete surface coverage. The generation of smooth and uniform FA(2) films exhibiting stronger emission and longer charge carrier lifetime paved the way for the fabrication of solar cells exhibiting high V cell of 1.42 V and a negligible hysteresis. Arguably, devices based on FA(2) FAPbBr3 films perform remarkably better owing to less shunting between TiO2 and spiro-OMeTAD, and reduced nonradiative losses. ASE studies on perovskite films showed that the FA(2) films themselves exhibit promising emission characteristics with a sharp transition from SE to ASE and a higher quantum yield along with a high quantum efficiency. Without any contextualization, we believe this work could lead to the fabrication of efficient FAPbBr3-based true green lasers in the future.

4. Experimental Section

Preparation of Photoanode and Device Fabrication: Prior to the deposition of TiO2 compact layer, the FTO substrate was cleaned by ultrasonication in Deconex (0.2% deionized H2O) detergent, rinsed thoroughly with deionized water and ethanol, and then treated in a UV/O3 cleaner for 15 min with 5 min ramp time, 375 °C for 5 min with 5 min ramp time, 450 °C for 5 min with 5 min ramp time, 500 °C for 15 min with 5 min ramp time) in dry air.

Synthesis of CH(NH2)2Br: CH(NH2)2Br was synthesized by dropping slowly 15 mL of hydrobromide acid (48% wt. in water) (Aldrich) into a solution of 5 g formamidine acetate (Sigma-Aldrich) in methanol cooled at 0 °C. The solution was further stirred for 5 h at room temperature and then at 80 °C for 30 min. The clear solution was concentrated by rotary evaporation at 80 °C until no obvious liquid remained. Subsequently the crude solid was dissolved by a minimum amount of ethanol and reprecipitated in diethyl ether and filtered. The procedure was repeated three times and the resulting white solid was collected and dried at 80 °C under vacuum.

Deposition of FAPbBr3 Perovskite: All materials were purchased from Sigma-Aldrich or Acros Organics and were used as received. FAPbBr3 films were deposited using sequential deposition method. 1.2 M PbBr2 precursor solutions were prepared in DMF and DMSO by constant stirring at 60 °C for 30 min. PbBr2 (DMF), PbBr2 (DMF+DMSO in 1:1 volume ratio) and PbBr2 (DMSO) solutions were spin coated on the mesoporous TiO2 films at 3000 rpm for 30 s. This was followed by annealing the films at 80 °C for 15 min. After cooling to room temperature, the films were dipped into isopropanol solution of FABr (50 x 10−3 M) for 5 min at 60 °C, rinsed with 2-propanol for 5 s and dried at 80 °C for 30 min.

Deposition of Hole Conductor and Device Fabrication: To complete the fabrication of devices, spiro-OMeTAD as HTM was deposited by spin coating 40 µL of the prepared solution at 4000 rpm for 30 s. The HTM solution was prepared by dissolving 72.3 mg (2,2′,7,7′-tetakis(N,N-di-methoxyphenylamine)-9,9-spirofluorene) (spro-OMeTAD), 17.5 µL of a stock solution of 520 mg mL−1 bis(trifluoromethylsulfonyl)imide in acetonitrile, and 29 µL of a stock solution of 300 mg mL−1 tris-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III)-bis(trifluoromethylsulfonyl)imide in acetonitrile, and 28.8 µL 4-tert-butylpyridine in 1 mL chlorobenzene. The device fabrication was carried out under controlled atmospheric conditions with humidity <1%. Finally, device fabrication was completed by thermally evaporating 70 nm of gold layer as a back contact.

Materials and Spectroscopic Characterization: XRD data were collected on aBruker Advance D8 X-ray diffractometer with a graphite monochromator, using Cu-Kα radiation, at a scanning rate of 0.5° min−1. An FESEM (Merlin) was employed to analyze the morphology of the samples. An electron beam accelerated to 3 kV was used with an in-lens detector. The optical properties of perovskite films were studied using UV–vis absorption and fluorescence spectroscopy. The absorption spectra of perovskite films were recorded with a UV–vis–NIR spectrophotometer (CARY-5) in the transmission mode. To record phosphorescence spectra and PL decay kinetics, the samples were excited by the second harmonic of a picosecond mode-locked Ti:Sapphire laser (80.5 MHz). The excitation beam is focused on the sample by means of a 90 mm focal that allows for an excitation spot diameter of around 100 µm. The average power was kept in the range 1–10 mW, which corresponds to 0.05–0.5 µJ cm−2 per pulse. The collected PL was spectrally and temporally analyzed using a 32 cm focal length monochromator equipped with a charge-coupled device (CCD) and a streak camera. Power-dependent PL and ASE studies were carried out using picosecond laser pulses generated using an optical parametric generator (OPO) that is pumped by a Q-switched picosecond Nd:Yag laser with a fundamental output of 1064 nm, pulse duration of 70–80 ps and repetition rate of 15 Hz. The circular laser beam, after passing through the OPG, was focused using a biconvex lens to a diameter of 2 mm.

Device Characterization: The current–voltage characteristics of the perovskite devices were recorded with a digital source meter (Keithley model 2400, USA). A 450 W xenon lamp (Oriel, USA) was used as the light source for photovoltaic (J–V) measurements. The spectral output of the lamp was filtered using a Schott K113 Tempar sunlight filter (Praezision Glas & Optik GmbH, Germany) to reduce the mismatch between the simulated and actual solar spectrum to less than 2%. The photoactive area of 0.16 cm2 was defined using a dark-colored metal mask. Incident photon-to-current conversion efficiency (IPCE) measurements were made using a 300 W xenon light source (ILC Technology, USA). A double-monochromator spectrometer (Gemini-180, Jobin Yvon Ltd., UK) was used to select and increment the wavelength
of the radiation impinging on the cells. The incident monochromatic light was passed through a chopper running at 1 Hz and the on/off ratio was measured by an operational amplifier. This was superimposed on a white light bias corresponding to an intensity of 10 mW cm⁻². IS, electroluminescence and intensity-dependent photovoltage measurements were performed by a Biologic SP300 (BioLogic, France). The measurements were performed with white light emitting diodes (LEDs) with the intensity of about 1 sun. IS measurements were carried out in a frequency range between 7 MHz and 0.05 Hz for potentials between 0 V and about V_{oc} (with a 20 mV sinusoidal AC perturbation) in 50 mV steps. The resulting impedance spectra were analyzed with the ZView software (Scribner Associate).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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