Generic water-based spray-assisted growth for scalable high-efficiency carbon-electrode all-inorganic perovskite solar cells

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Highlights
Water-based spray-assisted growth is proposed for all-inorganic perovskite films
Water solvent makes perovskite films immune to microstructure of lead halide films
Record-high PCE of 10.22% is achieved for carbon-electrode CsPbBr$_3$ PSC
High PCEs are also attained for carbon-electrode CsPbCl$_3$, CsPbI$_2$Br, and CsPbI$_3$Br PSCs

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This work
Carbon-electrode CsPbBr$_3$ PSCs
Generic water-based spray-assisted growth for scalable high-efficiency carbon-electrode all-inorganic perovskite solar cells

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SUMMARY
A water-based spray-assisted growth strategy is proposed to prepare large-area all-inorganic perovskite films for perovskite solar cells (PSCs), which involves in spraying of cesium halide water solution onto spin-coating-deposited lead halide films, followed by thermal annealing. With CsPbBr3 as an example, we show that as-proposed growth strategy can enable the films with uniform surface, full coverage, pure phase, large grains, and high crystallinity, which primarily benefits from the controllable CsBr loading quantity, and the use of water as CsBr solvent makes the reaction between CsBr and PbBr2 immune to PbBr2 film microstructure. As a result, the small-area ($0.09 \text{ cm}^2$) and large-area ($1.00 \text{ cm}^2$) carbon-electrode CsPbBr3 PSCs yield the record-high efficiencies of 10.22% and 8.21%, respectively, coupled with excellent operational stability. We also illustrate that the water-based spray-assisted deposition strategy is suitable to prepare CsPbCl3, CsPbBr2, and CsPbI2Br films with outstanding efficiencies of 1.27%, 10.44%, and 13.30%, respectively, for carbon-electrode PSCs.

INTRODUCTION
Perovskite solar cells (PSCs) have emerged as a promising candidate for photovoltaic power systems as per their high efficiency, low-cost raw materials, and straightforward fabrication process (Kojima et al., 2009; Park and Zhu, 2020; Rong et al., 2018). Their certified power conversion efficiency (PCE) of more than 25%, together with their enormously improved operational reliability, makes them particularly attractive (Li et al., 2021; Liu et al., 2021). However, the state-of-the-art PSCs are fabricated with organic-inorganic hybrid perovskite materials that contain volatile organic cations such as methylammonium (MA+) or formamidinium (FA+), which inherently result in the poor thermostability and photostability of resulting PSCs (Cheng and Ding, 2021; Chi and Banerjee, 2021; Li et al., 2020). Accordingly, researchers have shifted their attention toward all-inorganic perovskite alternatives (e.g., CsPbX3, X = I, Br, Cl, or their mixtures) that are more robust against thermal and light stresses (Faheem et al., 2019; Ho-Baillie et al., 2019; Tian et al., 2020). In this way, carbon-electrode, all-inorganic PSCs have been proposed based on all-inorganic perovskite materials, which are free of organic, mutable hole-transporting layers and noble metal electrodes, thus possessing significant advantages in terms of production cost and stability (Duan et al., 2018b; Liang et al., 2016; Tian et al., 2020).

All-inorganic perovskite materials investigated for carbon-electrode, all-inorganic PSCs mainly include CsPbI3 (Wang et al., 2021; Xiang et al., 2018, 2019), CsPbI2Br (Dong et al., 2019; He et al., 2020; Lin et al., 2020; Zhu et al., 2021), CsPbBr2 (Du et al., 2021; Zhu et al., 2018), and CsPbBr3 (Chang et al., 2016; Duan et al., 2018b), and the performance of resulting carbon-electrode, all-inorganic PSCs has advanced rapidly in recent years. To be specific, since the first report of carbon-electrode CsPbBr3 PSC in 2016 (Chang et al., 2016), its PCE has been promoted from 5.0% to 10.85% (Chang et al., 2016; Duan et al., 2020). When a hole booster composed of graphene oxide and (NiCo)1-yFeyOx is adopted, the PCE of carbon-electrode CsPbI2Br PSC can reach up to 10.95% (Du et al., 2021). We demonstrated a top-seeded growth strategy in our laboratory which enables carbon-electrode CsPbBr3 PSC with a record-high PCE of 14.84% (Zhu et al., 2021). Superior operational stability has also been demonstrated in carbon-electrode,
all-inorganic PSCs. For example, Qi et al. (Tong et al., 2019a) reported a carbon-electrode CsPbBr3 PSC that can retain 80% of its initial efficiency in ambient air for more than 2000 h without any encapsulation. When the surface of CsPbI3Br film is modified by hexyltrimethylammonium bromide (HTAB), the resulting PSC maintains 94% of the initial PCE after 2350-h storage and up to 90% of the initial PCE after aging for 330 h in a high-temperature (85°C) and medium-humidity (40%-60%) environment (Zhang et al., 2021). These significant achievements support the potential of carbon-electrode, all-inorganic PSCs for further development and practical applications.

Perovskite films with full coverage, enough thickness, pure phase, high crystallinity, and good uniformity are desired to fabricate large-area, high-efficiency PSCs for commercialization, either in a conventional or carbon-electrode configuration (Lee et al., 2020; Park and Zhu, 2020). The requirements for coverage, thickness, crystalline phase, and crystallinity guarantee high PCEs of resulting PSCs. Good uniformity is important to reduce the PCE gaps between the large-area PSCs and small-area ones, wherein it is generally necessary for large-scale (>800cm²) PSCs to achieve similarly high PCEs with small-area PSCs for commercialization (Hu et al., 2019; Qiu et al., 2019). Some PCE loss is inevitable when the solar cell or module area increases, which is a more serious problem for PSCs than for other photovoltaic cells (Li et al., 2018). This disparity largely results from the fact that most of the PSCs are fabricated via spin coating method. This approach is not suitable for preparing the large-area, uniform perovskite films required for commercialization (Park and Zhu, 2020). This inapplicability is more prominent in inorganic perovskite films, as the solubilities of their precursor lead halide and cesium halide salt materials vary significantly in frequently used aprotic solvents such as dimethyl sulfoxide (DMSO) and N, N dimethylformamide (DMF) (Chen et al., 2020; Duan et al., 2018b; Sutton et al., 2016). Thus, the synthetic crystallization control of spin-coated films is not possible over large scales, and the non-uniformities in morphology and crystallinity become serious problems in large-area all-inorganic perovskite films (Chen et al., 2020). Meanwhile, spin coating must be conducted differently to produce inorganic perovskite films with different compositions, which makes the methodology for producing all-inorganic perovskite films extremely complex (Tian et al., 2020). Therefore, there is an urgent demand for a universal preparation strategy for large-area all-inorganic perovskite films with full coverage, high crystallinity, and good uniformity as the next step in securing effective, carbon-electrode, all-inorganic PSCs.

The spraying technique can be scaled up for large-area, uniform films, as is popular in the context of industrial manufacturing (Krebs, 2009). This upsampling dramatically increases the utilization rate of precursor materials. Such a promising technique has been developed to prepare large-area, all-inorganic perovskite films (Li et al., 2018; Park and Zhu, 2020; Remeika and Qi, 2018; Swartwout et al., 2019). However, the record PCE of resulting all-inorganic PSCs with the conventional configuration is only 13.82% for 112-cm² devices based on composition-graded CsPbI2Br/CsPbI3 Br, films (Heo et al., 2021). Moreover, the current spray deposition technology seems to require additional modification strategies to boost the performance of corresponding PSCs, as recently demonstrated by Liu et al. (Yu et al., 2021). On the other hand, the PCEs of carbon-electrode, all-inorganic PSCs fabricated by spraying are inferior. For example, spray-assisted deposition yielded a CsPbBr3 PSC with an active area of 1 cm² and PCE of only 4.12% in a previous study (Duan et al., 2018a). The best-performing CsPbBr3 PSC prepared by spray-based method shows a stabilized PCE of only 6.3% (Lau et al., 2016). In addition, the spraying-based methods are still just practicable to all-inorganic perovskite films with specific compositions (Duan et al., 2018a; Yu et al., 2021; Zhou et al., 2018). Therefore, breakthroughs are needed for all-inorganic perovskite films to be manufactured by a scalable, universal spraying technique for carbon-electrode, all-inorganic PSCs, requiring understanding and control over the composition chemistry, fluid dynamics, and crystal growth behavior.

In this study, we developed a generic spray-assisted deposition strategy to produce all-inorganic perovskite films by innovatively adopting water as a benign solvent of cesium halide salts. Cesium halide solution is directly sprayed onto spin-coating-produced lead halide films under ambient conditions, followed by thermal annealing to promote the interdiffusion reaction between cesium halide and lead halide to form all-inorganic perovskite films. With CsPbBr3 as an example, we demonstrate that full-coverage, pure-phase, large-grain films can be prepared by adjusting the loading dose of CsBr/H2O solution, which enables small-area (0.09 cm²) carbon-electrode PSCs with optimized PCE of 10.22% and excellent operational stability. The use of water as the solvent of CsBr makes the reaction between CsBr and PbBr2 immune to the underlying PbBr2 film microstructure. Consequently, large-area, high-quality, uniform CsPbBr3 films can be obtained with resulting carbon-electrode PSCs having an active area of 1 cm² and PCE of 8.21%. The PCEs
we produced for both small- and large-area carbon-electrode CsPbBr₃ PSCs have the highest values among those with similar configurations reported previously. We explored the applicability of the water-based spray-assisted deposition strategy to prepare other all-inorganic perovskite films, wherein the well-crystalized, uniform CsPbCl₃, CsPbI₂Br, and CsPbI₂Br films were obtained with similar recipes at PCEs of up to 1.27%, 10.44%, and 13.30% for resulting carbon-electrode PSCs, respectively. The results of this work may provide a feasible approach to scalable, high-efficiency carbon-electrode, all-inorganic PSCs.

RESULTS

Preparation of CsPbBr₃ films

Typical all-inorganic perovskite CsPbBr₃ was adopted as an example to illustrate the feasibility of water-based spray-assisted deposition in realizing high-quality, large-area, uniform all-inorganic perovskite films. The strategy is schematically depicted in Figure 1A. First, 100 μL of 1 M PbBr₂ solution was spin-coated onto TiO₂/FTO substrate to produce the PbBr₂ film. Next, 30, 60, 90, 120, or 150 μL CsBr/H₂O solution was spread onto the PbBr₂ film. The film was dried at room temperature for 30 min to achieve a uniform CsPbBr₃ film.
Morphology and structure of CsPbBr₃ films

The morphologies of as-prepared CsPbBr₃ films were studied by scanning electron microscopy (SEM) as shown in Figures 1C–1G. For comparison, a SEM image of pristine PbBr₂ film is also provided in Figure 1B. The PbBr₂ film contains some randomly distributed pores, which support thorough contact of PbBr₂ with CsBr for complete transformation into CsPbBr₃ (Bing et al., 2020). As CsPbBr₃ formation is accompanied by the volume expansion of PbBr₂ film, these pores may release the micro-strain induced by volume expansion (Zhang et al., 2015). Pores and pinholes can still be observed in CsPbBr₃ films prepared with 30 and 60 μL of CsBr/H₂O, which indicates the incomplete conversion of PbBr₂ into CsPbBr₃. In other samples, the pores and/or pinholes disappear completely, resulting in CsPbBr₃ films composed of closely packed crystalline grains. The surfaces of CsPbBr₃ films formed with 90 and 120 μL of CsBr/H₂O are also relatively flat, while some surface bulges can be observed in the sample prepared with 150 μL of CsBr/H₂O. These bulge structures are presumed to be related to excess CsBr (Zhou et al., 2018). The average grain sizes are estimated to be 0.71, 0.80, 0.74, 0.69, and 0.64 μm for the CsPbBr₃ films prepared with 30, 60, 90, 120, and 150 μL of CsBr/H₂O (Figure S1), respectively, all of which are comparable with those of previously reported CsPbBr₃ films (Chang et al., 2016; Duan et al., 2018b). Thus, CsPbBr₃ films with full coverage, flat surface, and large grains can be obtained via the proposed water-based spray-assisted deposition method after optimizing the volume of CsBr/H₂O.

Crystalline structures of the as-obtained CsPbBr₃ films were studied by X-ray diffraction (XRD). Figure 2A shows the XRD patterns and the magnified XRD results in the region of 2θ ranging from 10° to 14°. Diffraction peaks at 15.07°, 21.50°, 26.34°, and 30.61° can be detected in all the CsPbBr₃ films in accordance with previously reported perovskite CsPbBr₃ materials (Chang et al., 2016; Duan et al., 2018a; Duan et al., 2020; Tong et al., 2019a). By comparison, the sample prepared with 90 μL of CsBr/H₂O possesses the most intense (100) peak, indicating the highest crystallinity among the film samples. The CsPb₂Br₅ impurity phase can be identified in the CsPbBr₃ samples with 30 and 60 μL of CsBr/H₂O (Zhang et al., 2018), while the Cs₄PbBr₆ impurity phase can be observed in the films prepared with 120 and 150 μL of CsBr/H₂O (left panel, Figure 2A) (Zhang and Lin, 2020). However, both CsPb₂Br₅ and Cs₄PbBr₆ are absent from the CsPbBr₃ film prepared with 90 μL of CsBr/H₂O, which may be attributable to its relatively high crystallinity. The aforementioned XRD results make known that the pure-phase, high-crystallinity CsPbBr₃ film can be obtained by the proposed water-based spray-assisted growth strategy using 90 μL of CsBr/H₂O.

In CsPbBr₃ films, the formation of a CsPb₂Br₅ impurity phase is mainly caused by CsBr deficiency, while the Cs₄PbBr₆ impurity phase is largely related to excess CsBr, as shown in Figure 2B (Duan et al., 2018b; Zhang and Lin, 2020; Zhang et al., 2018). CsPbBr₃ and/or CsPb₂Br₅ impurity phases are generally found in CsPbBr₃ films owing to the inherent difficulty of precise control over the CsBr dose (Duan et al., 2018b; Feng et al., 2020). These impurity phases generate undesirable energy barriers and trap states which hinder the transport and extraction of charge carriers and drive down PSC performance. CsPbBr₃ PSC performance is limited owing to this obstacle. In this study, we precisely controlled the loading amount of CsBr by adjusting the volume of CsBr/H₂O based on the water-based spray-assisted growth strategy. Our results show that this solution-processed CsPbBr₃ film is suitable for practical applications.

Optical properties of CsPbBr₃ films

Figure 2C gives ultraviolet-visible (UV-vis) absorption spectra of the CsPbBr₃ films. A consistent absorption onset wavelength of ~523 nm and an exciton absorption peak at 509 nm can be observed for all films, which indicates that they have a similar bandgap of ~2.37 eV. The absorption values increase for the CsPbBr₃ films prepared with 30, 60, and 90 μL of CsBr/H₂O and then decrease for the samples obtained with 120 and 150 μL of CsBr/H₂O. The increased absorption intensities for the films produced with 30, 60, and 90 μL of CsBr/H₂O can be assigned to suppress or even eliminate CsPb₂Br₅ impurity phase, while the decreased absorption values for the samples prepared with 120 and 150 μL of CsBr/H₂O are largely related to the Cs₄PbBr₆ impurity phase they contain. CsPb₂Br₅ or Cs₄PbBr₆ impurity phases hold the bandgaps above 2.9 eV, so the films containing them have lower absorption intensities (Feng et al., 2020; Zhang and Lin, 2020; Zhang et al., 2018). Overall, the sample produced with 90 μL of CsBr/H₂O possesses the most intense absorption as it is composed of pure-phase CsPbBr₃, as the XRD results also suggest.
Figure 2D shows the steady-state photoluminescence (PL) spectra of the CsPbBr$_3$ films grown on insulating substrates. A PL peak at ~522 nm can be detected in each of the films, which mainly originates from the band-to-band radiative recombination of photogenerated charge carriers. The PL peak intensifies in sequence for the CsPbBr$_3$ films prepared with 30, 60, and 90 μL CsBr/H$_2$O and then weakens gradually for those obtained with 120 and 150 μL CsBr/H$_2$O. In this case, the sample produced with 90 μL CsBr/H$_2$O shows the highest PL peak intensity, which is indicative of the weakest non-radiative recombination of charge carriers it contains as well as its lack of impurity phase (Luo et al., 2020).

Solar cell performance
Carbon-electrode, all-inorganic PSCs were fabricated by following the layer stackings of FTO/TiO$_2$/CsPbBr$_3$/carbon to explore the photovoltaic performance of CsPbBr$_3$ films prepared with different doses of CsBr/H$_2$O. Figure 3A shows the SEM image of a representative PSC, where all the functional layers can be identified clearly. The thickness of CsPbBr$_3$ film is estimated to be ~340 nm, which is similar to that of previously reported CsPbBr$_3$ films prepared by two-step or multi-step methods (Chang et al., 2016; Duan et al., 2018b; Feng et al., 2020). Figure 3B gives the statistical PCEs of 20 individual carbon-electrode CsPbBr$_3$ PSCs fabricated with 30, 60, 90, 120, and 150 μL of CsBr/H$_2$O, the average PCEs of which are (4.37 ± 0.55)%, (6.96 ± 0.29)%, (9.34 ± 0.43)%, (7.71 ± 0.55)%, and (5.86 ± 0.36)%, respectively. The water-based spray-assisted growth strategy appears to be highly feasible to fabricate high-efficiency carbon-electrode CsPbBr$_3$ PSCs after the volume of CsBr/H$_2$O solution is optimized.
Figure 3C shows the current density versus voltage (J–V) curves of the best-performing carbon-electrode CsPbBr3 PSCs fabricated with different volumes of CsBr/H2O solution, which were measured under simulated AM 1.5 G illumination and voltage scanning from 1.7 to −0.2 V. The resulting photovoltaic parameters, including Jsc, Voc, FF, and PCE, are given in Table S1. The PCEs of related carbon-electrode CsPbBr3 PSCs improve as CsBr/H2O dose increases from 30 to 90 μL. The value then decreases once the dose exceeds 90 μL. Variations in Jsc, Voc, and FF follow the same trend with CsBr/H2O dose. Thus, the carbon-electrode CsPbBr3 PSCs fabricated with 90 μL of CsBr/H2O have the best photovoltaic parameters among the PSCs. More importantly, its PCE of 10.22% stands the best value achieved for carbon-electrode CsPbBr3 PSCs without any interface modification until now, as indicated by Table 1. The improved PCE of the carbon-electrode CsPbBr3 PSC with increased CsBr/H2O dose from 30 to 90 μL can be attributed to a reduction in pores and/or pinholes as well as CsPb2Br5 impurity phase in the CsPbBr3 film. The decreased PCE of CsPbBr3 PSC is attributable to the Cs4PbBr6 impurity phase that emerges in the film when CsBr/H2O dose exceeds 90 μL.

External quantum efficiency (EQE) spectra of the carbon-electrode CsPbBr3 PSCs are shown in Figure 3D, where an identical photocurrent onset wavelength of ~530 nm can be identified for all samples in
accordance with the absorption features of CsPbBr3 films. The photocurrents appear to be generated by CsPbBr3. EQEs in the whole response range are enhanced as CsBr/H2O dose increases from 30 to 90 mL and then begin to decline as the CsBr/H2O dose reaches 90 mL. The Jsc values integrated from the EQE spectra are 5.50, 6.43, 7.58, 7.25, and 6.27 mA/cm2 for the carbon-electrode CsPbBr3 PSCs prepared with 30, 60, 90, 120, and 150 mL CsBr/H2O, respectively, which basically agrees with the light J-V curve results.

The working stability of the typical carbon-electrode CsPbBr3 PSC prepared by 90 mL CsBr/H2O was estimated under simulated AM 1.5G illumination and in ambient air with relative humidity (RH) of ~45% and temperature of ~25°C. Figure 3E shows the normalized photocurrent output near the maximum power point over 16 h. The photocurrent output is quite stable, and 90% of the initial value can be maintained after continuous testing, revealing the excellent operational stability of the carbon-electrode CsPbBr3 PSC fabricated by the proposed strategy.

The proposed water-based spray-assisted growth strategy appears to enable full-coverage, pure-phase, large-grain CsPbBr3 films with an optimized CsBr/H2O volume of 90 mL, ultimately yielding carbon-electrode PSCs with record-high efficiency and excellent operational stability. The uniformity of PbBr2 film fabricated by the proposed method does not significantly influence the uniformity of the resulting CsPbBr3 film. We used three PbBr2 films with different uniformities to prepare respective CsPbBr3 films to confirm this, noting the PbBr2 films were prepared by adjusting the thermal treatment temperature to be 100°C, 150°C, and 200°C after the spin coating procedure. As shown in Figure 4A, PbBr2 films with different surface appearances produced similar CsPbBr3 films. In this case, a highly uniform CsPbBr3 film of 10 x 10 cm2 in size was prepared successfully as shown in Figure 4B. SEM images of the PbBr2 films and the corresponding CsPbBr3 films are shown in Figures 4C1–4C3 and 4D1–4D3. The microstructures of PbBr2 films differ significantly in terms of surface coverage and grain morphology, but the resulting CsPbBr3 films have comparable microstructures including uniform, flat, and closely packed crystalline grains with similar sizes. Thus, we conclude that the water-based spray-assisted growth strategy can effectively yield the large-area CsPbBr3 films with satisfactory crystalline quality.

We noted that the desirable characteristics of the water-based spray-assisted growth strategy can be attributed to the reconstruction of PbBr2 film induced by water solvent during spray-coating of CsBr/H2O. To support our standpoint, the PbBr2 films prepared with the thermal treatment temperature to be 100°C, 150°C, and 200°C were treated by directly spraying 90 uL of deionized water onto it, followed by annealing at 250°C for 5 min. The SEM images of the resulting PbBr2 films are shown in Figures S2A–S2C. It is seen that the clear surface reconstruction of PbBr2 film happens after the water treatment, which leads to the PbBr2 films having the similar morphologic characters. Therefore, the final CsPbBr3 films exhibit the alike surface appearances.

### Table 1. Summary of PCE, V_{oc}, J_{sc}, and FF values of carbon-electrode CsPbBr3 PSCs without any interface modification reported so far

| Cell configuration | Area (cm²) | V_{oc} (V) | J_{sc} (mA/cm²) | FF | PCE (%) | Ref. |
|--------------------|-----------|------------|-----------------|----|---------|------|
| FTO/TiO2/CsPbBr3/carbon | 0.09 | 1.528 | 8.06 | 0.83 | 10.22 | This work |
| FTO/TiO2/CsPbBr3/carbon | 1 | 1.397 | 7.84 | 0.75 | 8.21 | |
| FTO/TiO2/SnO2/CsPbBr3/carbon | 0.071 | 1.310 | 8.24 | 0.814 | 8.79 | Liu et al. (2019b) |
| FTO/c-TiO2/CsPbBr3/carbon | 0.09 | 1.460 | 9.24 | 0.754 | 10.17 | Tong et al. (2019b) |
| FTO/c-TiO2/CsPbBr3/carbon | 0.09 | 1.413 | 9.55 | 0.73 | 9.86 | Tong et al. (2019a) |
| FTO/c-TiO2/CsPbBr3/carbon | 0.09 | 1.520 | 7.28 | 0.805 | 8.86 | Zhang et al. (2019) |
| FTO/TiO2/CsPbBr3/carbon | 0.09 | 1.370 | 7.66 | 0.82 | 8.63 | Guo et al. (2019) |
| FTO/TiO2/CsPbBr3/carbon | 0.09 | 1.430 | 7.32 | 0.78 | 8.16 | Li et al. (2019) |
| FTO/TiO2/CsPbBr3/carbon | 0.12 | 1.240 | 7.4 | 0.73 | 6.70 | Liang et al. (2016) |
| FTO/c-TiO2/CsPbBr3/carbon | 0.09 | 1.380 | 7.13 | 0.62 | 6.1 | Li et al. (2019a) |
| FTO/TiO2/CsPbBr3/carbon | 0.09 | 1.340 | 6.46 | 0.68 | 5.86 | Teng et al. (2018) |
| FTO/c-TiO2/CsPbBr3/carbon | 0.12 | 1.130 | 6.79 | 0.70 | 5.38 | Luo et al. (2018) |
Figure 4. Photograph and morphology characterizations of PbBr₂ films and CsPbBr₃ films as well as photovoltaic performance of large-area carbon-electrode CsPbBr₃ PSCs

(A) Photographs of PbBr₂ films prepared with the different thermal treatment temperatures of 200°C, 150°C, and 100°C after the spin coating procedure, along with the CsPbBr₃ films prepared by water-based spray-assisted deposition.

(B) Photograph of CsPbBr₃ sample 10 × 10 cm² in size.

(C₁–C₃) SEM images of the PbBr₂ films with the thermal treatment temperature of (C₁) 200°C, (C₂) 150°C, and (C₃) 100°C.

(D₁–D₃) SEM images of CsPbBr₃ films produced with the PbBr₂ films with the thermal treatment temperature of (D₁) 200°C, (D₂) 150°C, and (D₃) 100°C.

(E) Statistical PCEs of 20 individual carbon-electrode CsPbBr₃ PSCs with active area of 1 cm².

(F and G) (F) J-V curve and (G) EQE spectrum for best-performing carbon-electrode CsPbBr₃ PSC with the active area of 1 cm².
Carbon-electrode CsPbBr$_3$ PSCs with a large active area of 1 cm$^2$ were also fabricated. Figure 4E shows the statistical PCEs of 20 PSCs obtained from five individual batches, wherein the average PCE is (6.77 $\pm$ 0.54)$\%$. The J-V curve of the best-performing large-area carbon-electrode CsPbBr$_3$ PSC is shown in Figure 4F; its J$_{sc}$, V$_{oc}$, FF, and PCE are 7.84 mA/cm$^2$, 1.397 V, 0.75, and 8.21$,\%$, respectively. Notably, as also shown in Table 1, the PCE achieved here exceeds those of all previously reported large-area carbon-electrode CsPbBr$_3$ PSCs. The EQE spectrum shown in Figure 4G is similar to the small-area sample, and the integrated J$_{sc}$ is in accordance with the J-V curve value, which validates the PCE test results from the J-V curves again.

We applied the proposed strategy to prepare other typical perovskite films for carbon-electrode, all-inorganic PSCs to explore its versatility. Similar to the optimized preparation recipe of CsPbBr$_3$ films, CsPbCl$_3$, CsPbI$_2$Br, and CsPbI$_2$Br films were prepared by spin coating of 90 mL of CsCl/H$_2$O, CsI/H$_2$O, and CsBr/H$_2$O onto PbCl$_2$, PbBr$_2$, and PbI$_2$ films, respectively. Photographs of the resulting films are given in the upper panel of Figure 5A. For comparison, photographs of the CsPbCl$_3$, CsPbBr$_2$, and CsPbI$_2$Br films prepared by the conventional two-step spin coating method are also provided in the bottom panel of Figure 5A. The color of the each of the films well consists with their bandgaps (Zhu et al., 2021; Zhu et al., 2020; Zhou et al., 2018). As expected, highly uniform CsPbCl$_3$, CsPbBr$_2$, and CsPbI$_2$Br films were obtained by the water-based spin-assisted growth strategy. The XRD patterns shown in Figure 5B reveal clear XRD peaks of (100), (110), and (200) planes in CsPbCl$_3$, CsPbBr$_2$, and CsPbI$_2$Br films, respectively, with no impurity phases. The UV-vis absorption spectra shown in Figure 5C indicate that CsPbCl$_3$, CsPbBr$_2$, and CsPbI$_2$Br films have absorption onsets of $\sim$420, 613, and 645 nm, which correspond to bandgap values of $\sim$2.95, 2.02, and 1.92 $eV$, respectively.

We also used the CsPbCl$_3$, CsPbBr$_2$, and CsPbI$_2$Br films to fabricate carbon-electrode, all-inorganic PSCs. The statistical PCEs of 20 independent PSCs based on CsPbCl$_3$, CsPbBr$_2$, and CsPbI$_2$Br films are shown in
Figure S3, wherein the average PCEs are (0.62 ± 0.22)%, (9.95 ± 0.23)%, and (12.54 ± 0.22)%, respectively. J-V curves of the best-performing PSCs based on CsPbCl3, CsPbIBr2, and CsPbI2Br films are shown in Figure 5D, and detailed photovoltaic parameters are given in Table S2. PCEs of 1.27%, 10.44%, and 13.30% were realized for PSCs fabricated with CsPbCl3, CsPbIBr2, and CsPbI2Br films, respectively, all of which rank among the highest-performing all-inorganic PSCs reported to date (Du et al., 2021; Zhu et al., 2021). In addition, the EQE spectra of the related PSCs in Figure S4 show that photocurrent onsets are well in accordance with the absorption characters of CsPbCl3, CsPbIBr2, and CsPbI2Br films, revealing that these inorganic perovskite films dominate their photoelectric conversion process. Overall, the aforementioned results make known that the proposed water-based spray-assisted growth strategy may be a universal approach to fabricating scalable, high-efficiency carbon-electrode, all-inorganic PSCs.

**DISCUSSION**

We developed a water-based spray-assisted growth method to prepare large-area all-inorganic perovskite films in this study. The proposed strategy is performed by directly spraying cesium halide water solution onto spin-coating-deposited lead halide films under ambient conditions, followed by thermal annealing. With CsPbBr3 as an example, we show that the films feature uniform surface, full coverage, pure phase, large grains, and high crystallinity after adjusting the volume of CsBr/H2O. These desired benefits of CsPbBr3 films mainly originate from the controllable CsBr loading and the use of water as the CsBr solvent, which makes the reaction between CsBr and PbBr2 immune to the underlying PbBr2 film microstructure. Small-area carbon-electrode CsPbBr3 PSCs with active area of 0.09 cm² yielded a PCE of 10.22% coupled with excellent operational stability in ambient air. We also achieved a PCE of 8.21% for the champion one with the aperture area of 1.00 cm². The PCEs we created for both small- and large-area CsPbBr3 PSCs stand the highest values among previously reported PSCs with a similar configuration, which are assumed to be further improved by element doping or interface modification strategies. We also demonstrated that the proposed water-based spray-assisted deposition strategy is applicable for desired CsPbCl3, CsPbIBr2, and CsPbI2Br films, with superior PCEs of 1.27%, 10.44%, and 13.30%, respectively, for carbon-electrode PSCs. We thus provide generic guidance for scalable, high-efficiency carbon-electrode, all-inorganic PSCs as well as further advancements in all-inorganic perovskite optoelectronics.

**Limitations of the study**

Here, a generic water-based spray-assisted deposition strategy to produce all-inorganic perovskite films is demonstrated to enable scalable, high-efficiency carbon-electrode, all-inorganic PSCs. However, owing to the toxicity of PbX2 (X = Cl, Br, or I) as well as its solvents, such as DMSO or DMF, PbX2 films can only be produced by spin coating in a glove box instead of using spray-assisted strategy in ambient air. Therefore, we can currently prepare a large-area CsPbBr3 film with a size of 10 × 10 cm², and the preparation conditions of the PbBr2 film limit the further scaling up of its size. Besides, the highest PCE of the large-area CsPbBr3 PSC prepared by proposed strategy was 8.21% lower than that of the small-area device, which was 10.22%. The deposition process for the larger area all-inorganic perovskite films and the performance optimization of PSCs based on them will be the direction of our continued research.

**STAR METHODS**

Detailed methods are provided in the online version of this paper and include the following:

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**SUPPLEMENTAL INFORMATION**

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2021.103365.
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AUTHOR CONTRIBUTIONS
W.Z. and C.Z. proposed and designed the experiments, J.Z. and Y.H. supervised the study, Z.Z. and Y.B. conducted the experiments, D.C. and J.M. performed the data collection, H.X. and D.C. fulfilled the analysis of experimental results, W.Z. and Z.Z. wrote the manuscript, and C.Z. and J.Z. helped to revise the manuscript. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| PbBr₂               | Alfa-Aesar | CAS: 10031-22-8 |
| PbI₂                | Alfa-Aesar | CAS: 10101-63-0 |
| CsBr                | Alfa-Aesar | CAS: 7787-69-1 |
| PbCl₂               | Xi’an Polymer Light Co., Ltd. | CAS: 7758-95-4 |
| CsCl                | Xi’an Polymer Light Co., Ltd. | CAS: 7647-17-8 |
| DMF                 | Sigma-Aldrich | CAS: 68-12-2 |
| Conductive carbon paste | Shanghai MaterWin New Materials Co., Ltd. | http://www.materwin.com/ |
| FTO glass           | Pilkington TEC Glass | https://www.p-oled.cn/index/zh-hans/ |

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Dr. Weidong Zhu (wdzhu@xidian.edu.cn).

Materials availability

This study did not generate new materials.

Data and code availability

All data reported in this paper will be shared by the lead contact upon request.

This paper does not report original code.

Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHODS DETAILS

Preparation of all-inorganic perovskite films

FTO substrate (2 × 2.5 cm²) was sequentially cleaned in detergent, deionized water, acetone, and ethanol with sonication, and finally were dried under N₂ stream. After further 15 min of ultraviolet ozone treatment, a ~60 nm of TiO₂ layer was deposited on FTO substrate by spin-coating of TiO₂ sol at 3000 rpm for 30 s and thermal annealing at 500°C for 1 h in air. Then, 100 µL of PbCl₂, PbBr₂, or PbI₂ solution was spin-coated onto TiO₂/FTO substrate at 2000 rpm for 30 s in a glovebox (pO₂, pH₂O < 1 ppm), wherein the PbCl₂, PbBr₂, or PbI₂ film was prepared by dissolving of 278 mg PbCl₂, 367 mg PbBr₂, and 461 mg PbI₂ into 1mL DMF at 90°C with vigorous stir. After the thermal treatment at 90°C for 30 min, the PbCl₂, PbBr₂, or PbI₂ film was obtained. Next, 90 µL of cesium halide water solution was sprayed onto lead halide film in ambient air by using a commercial airbrush, which was connected to N₂ gas with the pressure of 15 psi. To be specific, the 168 mg/mL CsCl/H₂O and PbCl₂ film were adopted to obtain the CsPbCl₃ film; the 250 mg/mL CsBr/H₂O and PbBr₂ was prepared by dissolving of 278 mg PbCl₂, 367 mg PbBr₂, and 461 mg PbI₂ into 1mL DMF at 90°C with vigorous stir. After the thermal treatment at 90°C for 30 min, the PbCl₂, PbBr₂, or PbI₂ film was obtained. The 236 mg/mL CsI/H₂O and PbI₂ were used to prepare the CsPbI₂Br film; the 260 mg/mL CsI/H₂O and PbBr₂ were employed to produce the CsPbI₂Br film; the 250 mg/mL CsBr/H₂O and PbBr₂ were utilized to form the CsPbI₂Br film. After the spray coating procedure, all the samples were annealed at 250°C for 5 min in ambient air to promote the reaction between cesium halide and lead halide.

Fabrication of carbon-electrode PSCs

Finally, the commercial conductive carbon paste was screen-printed onto the CsPbCl₃, CsPbBr₃, CsPbI₂Br, or CsPbI₂Br film in ambient air. The area of carbon paste pattern was fixed to be 0.09 or 1.00 cm². With the thermal treatment at 120°C for 15 min in ambient air, the carbon electrode can be formed, and hence a carbon-electrode, all-inorganic PCS can be achieved successfully.
Characterizations
SEM images were obtained by a Zeiss Supra-40 field-emission SEM instrument (Carl Zeiss SMT AG, Germany). XRD patterns were collected from the samples by a D8-advance X-ray diffractometer (Bruker, Germany). A PerkinElmer spectrophotometer was used to record the UV-visible absorption spectra. Steady-state PL spectra were obtained by a Delta Flex fluorescence lifetime system (Horiba Scientific Com., Japan) with an excitation at 478 nm. J-V characteristics were measured by a Keithley 2450 source-meter, during which the PSCs were placed under a simulated AM 1.5G irradiation generated by an Oriel 92251A-1000 solar simulator in ambient air. EQE data were acquired in ambient air by using a solar-cell spectral-response measurement system (Cornerstone 74004) equipped with a 150 W xenon lamp (Oriel).

QUANTIFICATION AND STATISTICAL ANALYSIS
To compare the device performance changes, the photovoltaic parameters reported in this work are the average values of multiple PSCs under the same conditions.