

# Improving the triple-cation perovskite solar cells by two-step deposition methods with perovskite seeds

P Phiromruk<sup>1,2</sup> and S Chatraphorn<sup>1,2\*</sup>

<sup>1</sup>Physics of Energy Materials Research Unit, Department of Physics, Faculty of Science, Chulalongkorn University, Phyathai Rd., Bangkok 10330, Thailand

<sup>2</sup>Thailand Center of Excellence in Physics, CHE, 328 Si Ayutthaya Rd., Bangkok 10400, Thailand

\*Corresponding author's e-mail: sojiphong.c@chula.ac.th

**Abstract.** As of recent years, triple-cation perovskite solar cells have received immense attention due to its superior efficiency and better stability comparing to the classic single-cation perovskite solar cells such as MAPbI<sub>3</sub> or FAPbI<sub>3</sub>. A triple-cation perovskite layer which has been used most recently is cesium-containing FAPbI<sub>3</sub>-based perovskite. One of decent approaches to fabricate the layer is spin-coating technique by using two-step deposition process in which mixed lead-halide and CsI precursor is firstly spin-coated onto a substrate, then organic cation solution is deposited on the lead-halide layer. In this work, the results show that the performance of the devices from this process is lower than expected that could be due to difficulty of cesium ion incorporation as a stabilizer for FAPbI<sub>3</sub>-based perovskite. Perovskite seeding growth is introduced to solve the problem where the process is slightly modified from conventional two-step deposition methods by adding small amount of perovskite seed precursor into PbI<sub>2</sub> solution. The concentration of the perovskite seed in PbI<sub>2</sub> solution was varied for 0, 7, 14 and 20% v/v. The highest average efficiency of 11.9% was obtained from 7% v/v seeding concentration. Furthermore, the device performance could be improved by using proper amount of chlorobenzene (CB) as an anti-solvent. The highest efficiency of 18.4% was achieved by using 30  $\mu$ l of chlorobenzene.

## 1. Introduction

Over the past decade, the improvement of perovskite solar cells has been incredibly astounding in which the power conversion efficiency (PCE) rose from 3.8% in 2009 to >20% in the recent years because of high absorption over the visible spectrum, long charge carrier diffusion length, as well as engineering composition [1,2]. Perovskite materials for solar cells have ABX<sub>3</sub> structure where A is an organic monovalent cation such as CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> (methylammonium: MA<sup>+</sup>), CH<sub>3</sub>(NH<sub>2</sub>)<sub>2</sub><sup>+</sup> (formamidinium: FA<sup>+</sup>), and Cs<sup>+</sup>, B is typically Pb<sup>2+</sup> and X is a halide ion ,e.g., I and Br<sup>-</sup>.

The conventional perovskite materials (MAPbI<sub>3</sub> and FAPbI<sub>3</sub>) have been studied and shown that the disadvantage of MAPbI<sub>3</sub> is that it is sensitive to heat and humidity [3-5], whereas FAPbI<sub>3</sub> appears to be a better option in comparison with MAPbI<sub>3</sub> due to lower band gap and greater thermal stability [5]. However, FAPbI<sub>3</sub> lacks structural stability, namely, it has two different structures at room temperature. One is photo-inactive hexagonal structure (yellow phase) and the other one is photo-active cubic structure (black phase). In addition, the black phase of FAPbI<sub>3</sub> only stabilizes at high temperature [6]. These problems could be fixed by adding small amount of MA ions as a stabilizer for black phase of FAPbI<sub>3</sub> [1] and the efficiency of double-cation perovskite, such as FA<sub>0.83</sub>MA<sub>0.17</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub>, reached

18% [7]. Nonetheless, there is the trace of yellow phase left in case of double-cation perovskite [1]. Triple-cation perovskite was introduced to solve the problem. The triple-cation perovskite  $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$  was fabricated by one-step deposition method and the PCE from this process exceeded 20% and remained stable at 18% for at least 250 hours at maximum power point tracking [1]. Latterly, some reports demonstrated that the performance of  $\text{FAPbI}_3$ -based devices from one-step deposition process are inferior to that of two-step deposition method [8].

In this work, the two-step deposition method is a process in which mixed lead-halide and CsI precursor is firstly spin-coated onto a substrate, then organic cation solution is deposited on the lead-halide layer. Instead of mixing CsI with organic cation salts in IPA, CsI was dissolved in DMF because of the low solubility of CsI. As a result, the efficiency from this process was considerably lower than expected due to the difficulty of cesium ion incorporation as a stabilizer for  $\text{FAPbI}_3$ -based perovskite and CsI might assemble with  $\text{PbI}_2$  and acquire  $\text{CsPbI}_3$ . Though  $\text{CsPbI}_3$  has an acceptable band gap of 1.73 eV, the photoactive perovskite phase is only stable at very high temperature (more than 300 °C) [1]. One also suggested that adding CsI directly with lead-halide solvent could lead to discrepancy in performance of the devices among batches resulting from poor perovskite nucleation [8]. Two-step deposition method with perovskite seeds could be used to assist cesium ions to stabilize the black phase of  $\text{FAPbI}_3$  [8]. This process resembles to the combination of one-step and two-step deposition methods. Perovskite seed precursor was separately prepared from  $\text{PbI}_2$  solution, then the perovskite seed precursor is added in  $\text{PbI}_2$  solution and the rest of the steps are the same as the conventional two-step deposition method.

## 2. Methodology

### 2.1. Materials preparation

For conventional two-step deposition method; 1 M of  $\text{PbI}_2$  and 0.14 M of  $\text{PbBr}_2$  were dissolved in mixed solvent (DMF: DMSO = 4:1 volume ratio) and stirred overnight at 70 °C. 1 M of CsI was dissolved in mixed solvent (DMF: DMSO = 4:1 volume ratio) then stirred overnight at room temperature and mixed in lead-halide solution. MAI and FAI organic cation salts were dissolved in 2-propanol with a concentration of 10 mg/ml and stirred overnight at room temperature. For two-step deposition method with perovskite seeds, 1.8725 g of  $\text{PbI}_2$  was dissolved in 1 mL DMF and 160  $\mu\text{L}$  DMSO and stirred overnight at 70 °C. Perovskite seed precursor was prepared by mixing  $\text{PbI}_2$  (1.2 M),  $\text{PbBr}_2$  (0.21 M), FAI (1.08 M), MABr (0.18 M), and CsI (0.14 M) in DMF: DMSO = 4:1 volume ratio then stirred at about 60 °C for 10 min and mixed in  $\text{PbI}_2$  solution to form  $\text{Cs}_{0.09}\text{FA}_{0.77}\text{MA}_{0.14}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$  perovskite seed. The seeding concentration in this work was 7, 14, and 20% v/v. The organic cation solution was obtained from FAI (8.3 mg), MABr (0.83 mg), and MACl (0.87 mg) salts dissolved in 1 ml of IPA and stirred overnight at room temperature. Also, 0.0723 g of Spiro-MeOTAD was dissolved in 1 ml of chlorobenzene and stirred overnight at room temperature. 28.8  $\mu\text{l}$  of 4-tert-butylpyridine(t-BP) and 17.5  $\mu\text{l}$  of Lithium bistrifluoromethanesul formamide (Li-TFSI) of which 0.52 g dissolved in 1 ml of acetonitrile were mixed in 1 ml of Spiro-MeOTAD and kept stirring for 3 hours before use.

### 2.2. Device fabrication

Fluorine-doped tin oxide (FTO)-coated glasses were cleaned by using detergent, deionized water, acetone, and 2-propanol, sequentially. Compact- $\text{TiO}_2$  film (~50 nm) was spin-coated on the FTO-glass at 3000 rpm for 30s, then the film was annealed for 30 min at 500 °C. Mesoporous- $\text{TiO}_2$  film (~250 nm), after that, was deposited on the cp- $\text{TiO}_2$  layer at 3000 rpm for 30s, the film was then heated at 500 °C for 30 min. Next, lead-halide layer was spin-coated on the substrate at the rate of 3000 rpm for 30s, then annealed at 70 °C for 20 min and cool down. To form the perovskite layer (~600 nm), organic cation solution was then spin-coated at 2000 rpm for 20s, and repeated again, then followed by 50  $\mu\text{l}$  of chlorobenzene (CB) while the substrate was still spinning. Next, the perovskite layer was placed on a hot plate at 140 °C for 10 min. After cooling down, Spiro-MeOTAD layer (~150 nm) was spin-coated on perovskite layer at 3000 rpm for 30s and kept overnight for oxidation of the Spiro-MeOTAD. All the

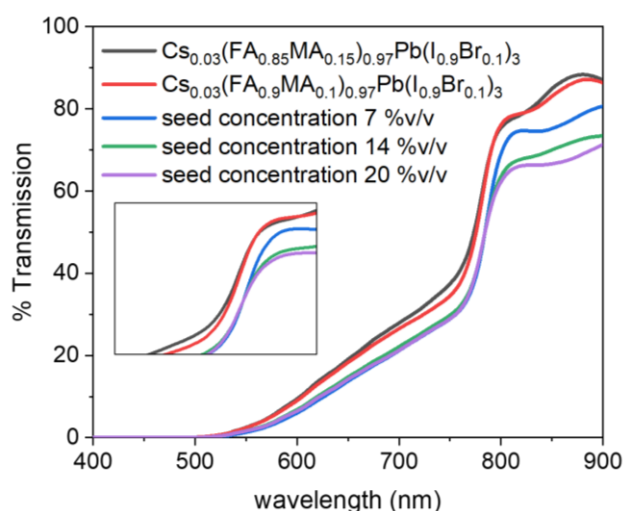
processes were carried out in N<sub>2</sub> filled glove box. Finally, 120 nm thick of Au contact was thermally evaporated on top of the spiro-MeOTAD layer.

### 2.3. Characterization

To study optical transmission and morphology of perovskite films, perovskite layer was deposited on FTO/Cp-TiO<sub>2</sub>/mp-TiO<sub>2</sub>. Cs<sub>0.03</sub>(FA<sub>0.90</sub>MA<sub>0.10</sub>)<sub>0.97</sub>Pb(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub> and Cs<sub>0.03</sub>(FA<sub>0.85</sub>MA<sub>0.15</sub>)<sub>0.97</sub>Pb(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub> films were obtained from conventional two-step deposition methods. For two-step deposition methods with perovskite seeds, the samples were prepared by PbI<sub>2</sub> solution with 0, 7, 14, 20% v/v seeding concentration. The optical transmission (%T) of perovskite films was examined by a spectrophotometer in the range of 350 – 1100 nm. Morphology of the perovskite films was characterized by a field-emission scanning electron microscope (FESEM; JEOL Model JSM-7001F). Solar cell parameters, e.g., PCE, fill factor (FF), short-circuit current density (J<sub>SC</sub>) and open-circuit voltage (V<sub>OC</sub>) were investigated under AM1.5 illumination by using Xe-lamp solar simulator and Keithley 238 source meter-unit and the active area of devices was 0.06 cm<sup>2</sup>.

## 3. Results and discussion

### 3.1. Optical transmission

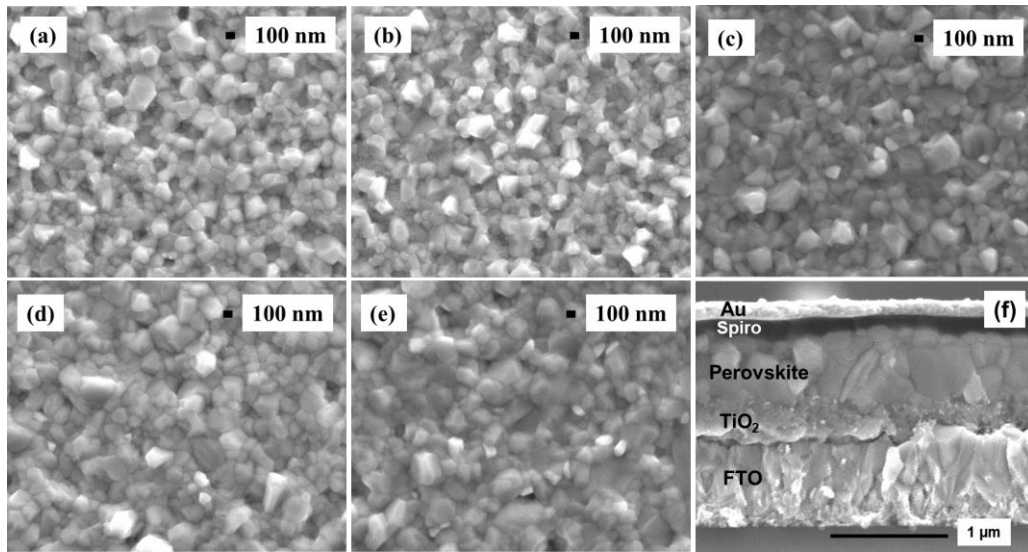


**Figure 1.** Optical transmission of perovskite films fabricated by two-step deposition method (black and red lines) and two-step deposition method with perovskite seeding concentration 7 (blue line), 14 (green line), and 20% v/v (purple line). [Inset shows the zone of absorption of perovskite films]

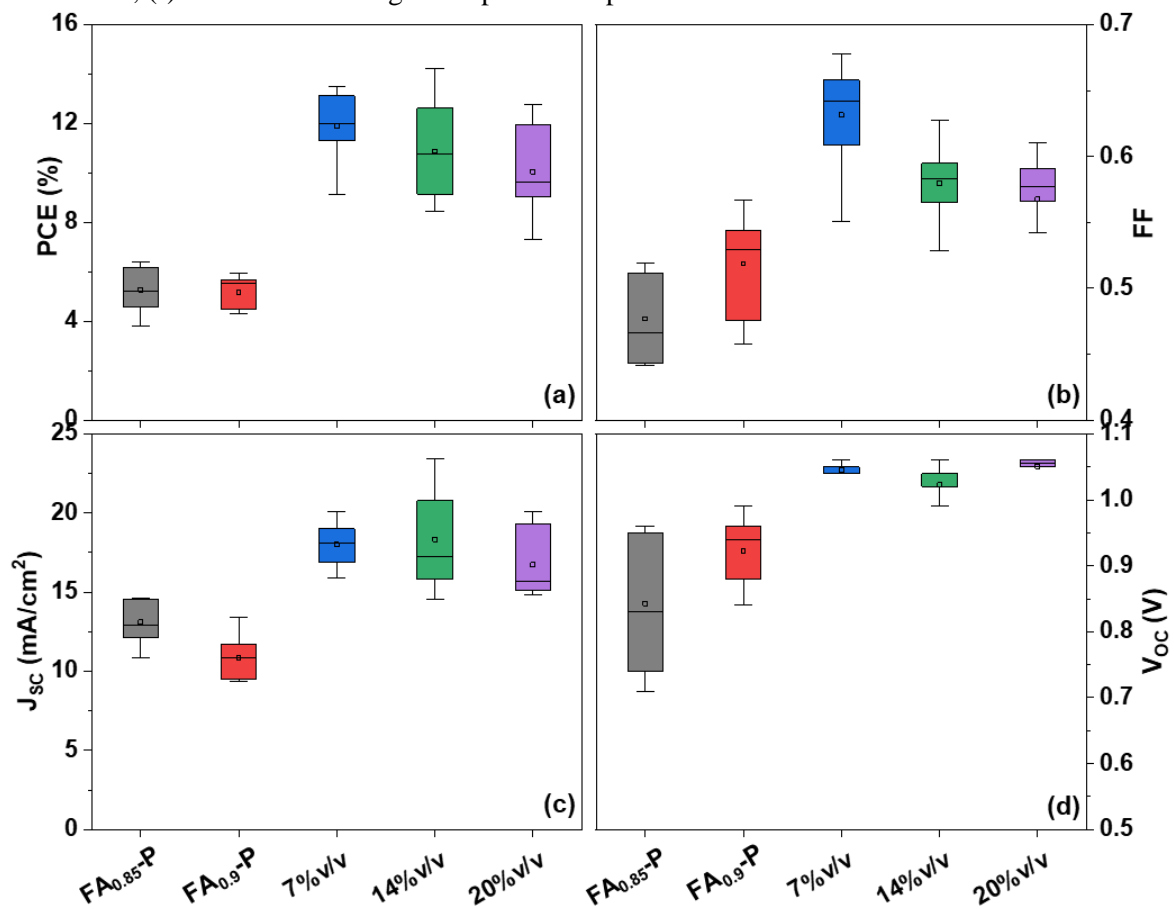
The optical transmission of perovskite films fabricated by traditional two-step deposition process (black and red lines) and two-step deposition process with perovskite seeds (blue, green, and purple lines) are plotted in figure 1. For the conventional process, the onset of optical absorption was observed at around 790 nm while it was slightly red shifted for the seeded-samples with the onset of optical absorption around 795 nm. The optical transmission of the samples from the new method are almost identical regardless of seeding concentration because very small amount of perovskite seeds was incorporated when compared to the content of the primary cations and halide ions. Thus, band gap energy among the seeded perovskite samples was unaltered.

### 3.2. Morphology

Figure 2 shows the surfaces of perovskite films fabricated by two-step deposition process (a) Cs<sub>0.03</sub>(FA<sub>0.85</sub>MA<sub>0.15</sub>)<sub>0.97</sub>Pb(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub> and (b) Cs<sub>0.03</sub>(FA<sub>0.90</sub>MA<sub>0.10</sub>)<sub>0.97</sub>Pb(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub> and two-step deposition process with seeding concentration (c) 7, (d) 14, and (e) 20% v/v. The grain shape and size from both methods were quite similar since the content of seeding concentration was very small as previously discussed. Even so, the seeded perovskite films looked denser and more compact causing smoother surface coverage for better contact between perovskite layer and hole transport layer and enhancing the



**Figure 2.** SEM images of perovskite films fabricated by two-step deposition method (a)  $\text{Cs}_{0.03}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.97}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$  and (b)  $\text{Cs}_{0.03}(\text{FA}_{0.90}\text{MA}_{0.10})_{0.97}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$  and 2-step deposition method with seeding concentration (c) 7, (d) 14, and (e) 20% v/v, (f) cross-section image of triple-cation perovskite solar cell.

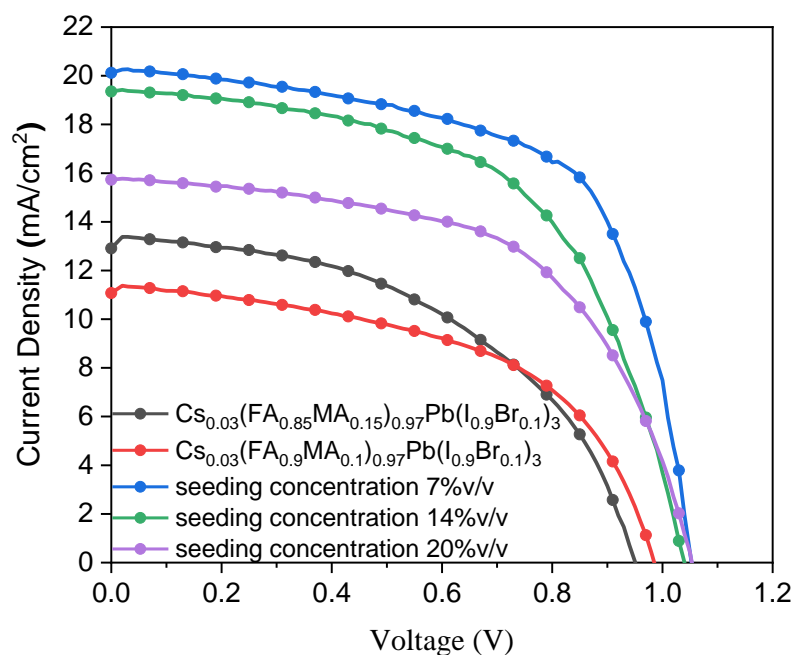


**Figure 3.** Box chart plots of solar cell parameter: (a) PCE, (b) FF, (c)  $J_{sc}$ , and (d)  $V_{oc}$  from two-step deposition method:  $\text{Cs}_{0.03}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.97}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$  (denoted as FA<sub>0.85</sub>-P) and  $\text{Cs}_{0.03}(\text{FA}_{0.90}\text{MA}_{0.10})_{0.97}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$  (denoted as FA<sub>0.9</sub>-P) and two-step deposition method with different seeding concentration. 50  $\mu\text{l}$  of CB is applied for both processes.

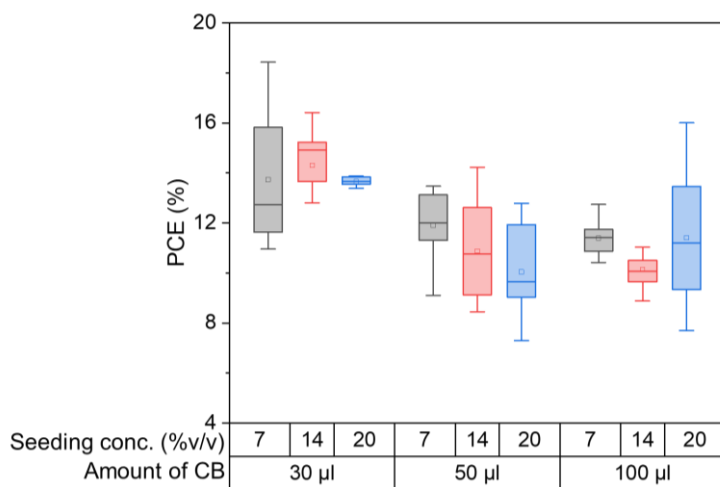
performance of the devices. The small amount of perovskite seed in  $\text{PbI}_2$  could help the nucleation of perovskite crystals and thus improved the crystal formation of the perovskite layer.

### 3.3. Solar cells parameters

J-V characteristics were investigated to obtain the solar cell parameters and are illustrated in figure 3. The grey and red box charts represent  $\text{Cs}_{0.03}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.97}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$  (denoted as  $\text{FA}_{0.85}\text{-P}$ ) and  $\text{Cs}_{0.03}(\text{FA}_{0.90}\text{MA}_{0.10})_{0.97}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$  (denoted as  $\text{FA}_{0.90}\text{-P}$ ) devices, respectively. The blue, green, and purple box charts represent devices from two-step method with different seeding concentration. The box charts indicate that the overall performance from conventional two-step deposition method was considerably poor comparing to that from two-step deposition method with perovskite seeds. For instance, the average PCE from the old method was only at 5.2%. On the other hand, the average PCE of 11.9% was from the two-step deposition method with seeding concentration 7% v/v. Also, short-circuit current density and open-circuit voltage, from perovskite seed process were clearly superior. The enhanced parameters of the seeded samples could be due to the improvement of the surface of perovskite films. Figure 4 shows the J-V curves of devices with best efficiency from each process. Furthermore, the amount of anti-solvent was found to be of importance as well. The use of chlorobenzene as anti-solvent of 30, 50, and 100  $\mu\text{l}$  were studied in the two-step deposition process with perovskite seeds. As shown in figure 5, the devices with 30  $\mu\text{l}$  of chlorobenzene yielded somewhat higher efficiency than devices with 50 and 100  $\mu\text{l}$  of chlorobenzene. The highest efficiency of 18.4% was attained from two-step deposition method with 7% v/v seeding concentration and the amount of 30  $\mu\text{l}$  of anti-solvent applied.



**Figure 4.** J-V curves of the best PCEs from two-step deposition method (black and red lines) and two-step deposition method with perovskite seed concentration 7 (blue line), 14 (green line), 20% v/v (purple line). 50  $\mu\text{l}$  of CB is applied for both processes.



**Figure 5.** Box chart plots of PCE from two-step deposition method with seeding concentration 7 (grey), 14 (red), and 20% v/v (blue) and different amount of anti-solvent.

#### 4. Conclusion

FAPbI<sub>3</sub>-based triple-cation perovskite solar cells were of interest because of its performance and stability and two-step deposition method was an intriguing option to fabricate such devices. The triple-cation perovskite films on ETL layer from two-step deposition method and two-step deposition method with perovskite seeds were studied. The optical transmission and morphology of perovskite films were not evidently affected by such processes apart from the fact that perovskite films from two-step deposition method with perovskite seeds were denser resulting in improved surface coverage. The PCE of devices from the seeding method yielded higher efficiencies compared to the conventional one because the crystal formation from PbI<sub>2</sub> to perovskite was enhanced by using two-step deposition method with perovskite seeds and the improved contact between perovskite layer and HTL. In addition, Cs in perovskite seeds could better stabilize the black phase of FAPbI<sub>3</sub>. It was also found that the suitable amount of anti-solvent could enhance the efficiency of devices from two-step deposition process with perovskite seeds. The best efficiency of 18.4% was obtained from two-step deposition method with 7% v/v seed concentration and the use 30 µl of chlorobenzene as anti-solvent.

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