Modified Antisolvent Method for Improving the Performance and Stability of Triple-Cation Perovskite Solar Cells

Mahmoud Samadpour,* Arezo Golchini, Karim Abdizadeh, Mahsa Heydari, Mozhdeh Forouzandeh, Zahra Saki, and Nima Taghavinia*

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1. INTRODUCTION

Increasing from 3.8% to more than 25% efficiency, hybrid organometallic halide perovskite solar cells (PSCs) have attracted excessive attention in recent years.1 Hybrid perovskites with an ABX3 structure, include an organic cation, A = methylammonium (MA) or formamidinium (FA), divalent metals, B = Pb2+ and Sn2+, and anions like X = Cl−, Br−, and I−.2–4 The high performance of PSCs have been ascribed to desirable properties such as a marked extinction coefficient, a tunable band gap, and the proper dynamics of charge transport at interfaces and whole devices.5–8 In spite of exponential increase in efficiency, still there are many concerns about the severe instabilities in perovskite solar cells. In addition to the characteristic of the hole/electron transport layers (HTLs/ETLs) and contacts, the stability of PSCs is mainly attributed to the perovskite layer properties.9–14 In this context, structural phase transition, light-induced trap states, halide segregation, and moisture/thermal-induced degradations have been widely investigated recently.15–18 Concerning the stability issue, a variety of novel HTLs/ETLs are introduced; also, a considerable research is conducted to make more stable, uniform, pinhole-free, and highly crystalline perovskite layers.19–28

For example, utilizing perovskites with mixed cations and halides not only improved the performance of the primary MAPbX3 perovskite layers but also increased the stability by hindering the volatile nature of MA molecules.23 Annealing-free vacuum-deposited perovskite absorbers were investigated by Zhao et al.24 Solvent-annealing was established as an effective route to improve the crystallinity, and the charge carrier diffusion length of trihalide perovskite materials was increased to over 1 μm.25,26 Sequential deposition is widely used as a route to high-performance perovskite-sensitized solar cells.27 More thermally stable with less phase impurities, perovskites were made by addition of inorganic cesium in triple-cation perovskite compositions.13 More recently flash infrared annealing has been utilized to improve the properties of the perovskite layers.28

Regarding the wet chemical deposition methods, numerous studies are performed to optimize the composition of solvents of perovskite precursors. As an instance, extremely uniform and dense perovskite layers were obtained by mixed solvent of γ-butyrolactone and dimethylsulphoxide (DMSO) followed by toluene drop-casting.29

Among the various approaches, the antisolvent technique is currently one of the most preferred methods to make highly crystalline, markedly smooth and pinhole-free perovskite layers.30–32 It is known that the quality of the perovskite layer is mostly directed by the nucleation and crystal growth stages. The antisolvent method produces many nuclei by abruptly reducing the precursor’s solubility following by crystal

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growth. Until now various antisolvent materials such as chlorobenzene, hexane, toluene, ethyl acetate, diethyl ether, isobutanol, isopropyl alcohol, and chloroform are utilized and investigated in details.\(^33-36\) Among the large number of possible antisolvents, chlorobenzene is much widely utilized solvents were utilized to make more homogeneous perovskite formation in the antisolvent method. For instance, mixed solvents were utilized to make more homogeneous perovskite layers.\(^37,38\) Through PMMA addition into the chlorobenzene/toluene, not only the electronic quality of perovskite layers was exponentially improved, but also the stability was improved remarkably.\(^41\)

Recently tetra ethyl orthosilicate (TEOS) was directly added in the precursor solutions of the perovskite and spin coated on the TiO\(_2\) substrates by Zhou et al.\(^42\) Their results indicated that silica encapsulates the grain boundaries of the perovskite layer and improves the efficiency and stability of cells. In spite of the superior properties, the explained method is applicable to the perovskite layers with formamidinium-based structures.

After that various research studies utilized TEOS antisolvent in order to modify the simple MAPbI\(_3\) structures in both planar n-i-p and p-i-n structures.\(^43,44\) Despite the improved photovoltaic properties, the intrinsic structural and thermal instability, in addition to the severe degradation of MAPbI\(_3\) structures upon contact with moisture, hinders the practical applications.\(^45\)

In this work, we have introduced a modified chlorobenzene (CB) antisolvent procedure for enhancing the performance of the triple-cation perovskite active layers by improving their electronic properties. Here, TEOS was incorporated into the CB antisolvent, in order to decrease the surface defects during the fast nucleation and growth of perovskite grains. A remarkable decrement in surface trap states of perovskite layers were confirmed through highly enhanced photocurrent density of the pristine and modified perovskite layers. This was further confirmed by studying the capacitive properties of the perovskite layer between the contacts by electrochemical impedance spectroscopy (IS) measurements. In addition to the improved photovoltaic properties, more stable devices were obtained by the proposed antisolvent method.

2. RESULTS AND DISCUSSION

With regards to the hydrolysis and condensation reactions in the presence of distilled water in antisolvent, TEOS will turn into silica gel according to the following reactions as explained elsewhere.\(^35\)

\[
\text{SiC}_n\text{H}_{2n+4}\text{O}_4 + n\text{H}_2\text{O} \Leftrightarrow n\text{Si(OH)}_n + 4\text{C}_2\text{H}_4\text{O}\H
\]

\[
\begin{align*}
n \text{SiC}_n\text{H}_{2n+4}\text{O}_4 & + n \text{Si(OH)}_n \\
& \Leftrightarrow (-\text{SiO}_2)_n + 4n \text{C}_2\text{H}_4\text{OH}
\end{align*}
\]

\[
\begin{align*}
n \text{Si(OH)}_n & + n \text{Si(OH)}_4 \\
& \Leftrightarrow (-\text{SiO}_2)_n + n \text{H}_2\text{O}
\end{align*}
\]

It is noteworthy that antisolvent pouring induces a considerable drop in the solubility of the perovskite precursors, providing a high density of nucleation sites followed by an effective crystal growth. With regards to the TEOS-incorporated antisolvents, crystallization of the perovskite grains and the precipitation of silica will take place simultaneously. Therefore, the dynamics of the perovskite crystallization could be affected by the silica oligomers in the antisolvent.

The crystalline structure of the pristine and modified perovskite films was characterized by X-ray diffraction (XRD), as illustrated in Figure 1. The diffraction peaks at 14.10, 20.03, 24.56, 28.43, 31.86, 40.64, and 43.28° corresponding to the crystalline planes of the photovoltaic black phase of the Cs\(_0.05\)(MA\(_{0.17}\)FA\(_{0.83}\))\(_3\)Pb(I\(_{0.83}\)Br\(_{0.17}\))\(_3\) perovskite layer.\(^13\)

Meanwhile, there is no diffraction peak from the undesired photo-inactive delta phase of FAPbI\(_3\) at 11.61°, which is a common and not preferred side structure in three cationic perovskite layers. This could be originated by Cs ions as explained before.\(^13\) The full width at half maximum (FWHM) of the main perovskite peak at 14.10° was obtained through fitting and was very similar, 0.19 and 0.20, respectively, for reference and TEOS-modified perovskite layers. The crystallite size of the perovskite layers estimated by the Scherrer equation from the most intense peak at 14.1° slightly reduced from 43 to 40.2 nm. Regarding the same position of perovskite diffraction peaks in reference and modified perovskite (PS) layers and a mere difference of FWHM, the provided results indicate that the structure of the PS film remained unchanged after the mentioned modification. This could propose the same antisolvent crystallization processes in both reference and modified antisolvents.

In addition to the fluorine-doped tin oxide (FTO)/TiO\(_2\) diffraction patterns, cubic PbI\(_2\) peaks were distinguished at both pristine and modified perovskite layers with a mere difference in intensity, which could be from the incomplete conversion of precursors to the black perovskite phase as the deposition is performed in an atmosphere environment here. It is known that PbI\(_2\) could passivate the defects and enhance the device performance, nevertheless excessive PbI\(_2\) content in the films adversely distress device performance by its poor optoelectronic properties.\(^36\) Furthermore, no diffraction patterns of incorporated silica were identified. This reveals that amorphous silica is integrated with the perovskite layer through the hydrolysis reaction of TEOS.

Concerning the morphology, scanning electron microscopy (SEM) images of the pristine and TEOS-modified perovskite layers in two different scales are provided in Figure 2. Apparent from this figure, a negligible difference could be observed in

![Figure 1. XRD spectra of pristine and modified perovskite films on FTO-coated glass/TiO\(_2\) substrates. Perovskite, PbI\(_2\), and FTO/TiO\(_2\) diffraction peaks are indicated by α, n, and δ, respectively.](https://dx.doi.org/10.1021/acsomega.0c04058)
surface morphology and large grain sizes are evident in both layers with or without TEOS modifications.

![Figure 2](image)

**Figure 2.** SEM image of (a, b) pristine and (c, d) TEOS-modified PS layers. Scale bar is 1 micron in figures (a, c) and 200 nm in figures (b, d).

According to the elemental mapping of the perovskite layer, Si is distributed in the whole layer (**Figure 3**), which indicates that an amorphous silica has encapsulated the entire perovskite layer while just a grain boundary encapsulation was observed through adding TEOS to perovskite precursors.42

Moreover, the ultraviolet–visible (UV–vis) absorption spectra of perovskite films were measured and are presented in **Figure 4a**. A glance at the given figure reveals a mere difference between the pristine and modified PS films absorption spectrum. Furthermore, concerning the Tauc plot shown in **Figure 4b**, the pristine and TEOS-modified PS band gaps are comparable, approximately 1.61 eV for both structures. These observations reveal that the TEOS modification has no marked effect on the Cs$_{0.05}$ (MA$_{0.17}$ FA$_{0.83}$)$_{0.95}$ Pb (I$_{0.83}$ Br$_{0.17}$)$_3$ PS layer in terms of the optical properties.

In order to explore the effect of TEOS-modified perovskite layers on the photovoltaic properties of PSCs, here reference and TEOS-modified cells were prepared. **Figure 5**, indicates the J–V curves of solar cells which are made with chlorobenzene (reference cells which are denoted by R-Cell) and TEOS-modified antisolvent (M-Cells). Here, antisolvent dripped from the solutions which are stirred in various time intervals after TEOS addition (1–50 min).

![Figure 5](image)

**Figure 5.** J–V curves of solar cells which are made with chlorobenzene (reference cells which are denoted by R-Cell) and TEOS-modified antisolvent (M-Cells). Here, antisolvent dripped from the solutions which are stirred in various time intervals after TEOS addition (1–50 min).

![Figure 4](image)

**Figure 4.** (a) UV−vis absorption spectra of the reference and TOES-modified Cs$_{0.05}$ (MA$_{0.17}$ FA$_{0.83}$)$_{0.95}$ Pb (I$_{0.83}$ Br$_{0.17}$)$_3$ film. (b) Tauc plots derived from absorbance spectra of pristine and modified PS films.
cells are summarized in Table 1, concerning an apparent explanation. According to the results provided, an open circuit voltage ($V_{oc}$) of 1.03 V, a short circuit current ($J_{sc}$) of 22.32 mA/cm$^2$, a fill factor (FF) of 62.49%, and a power conversion efficiency (PCE) of 14.36% are obtained in R-cells. It is noteworthy that our cells are made under the ambient environment and their efficiency is expected to be lower than the record efficiencies of more than 20% of triple-cation perovskite solar cells which are made under inert atmospheres like N$_2$ or Ar.13 The modified cell, with 2 min stirring time reveals a higher $J_{sc}$ of 22.78 mA/cm$^2$, $V_{oc}$ of 1.03 V, and a considerably raised FF of 71.25%, resulting in an improved efficiency of 16.72%.

A glance at the graph and Table 1 reveals the superior photovoltaic properties of modified cells in comparison to pristine ones, primarily the significant increase in the FF (from 62.49% in R-Cells to 71.25% in optimized M-cells) while the $V_{oc}$ and $J_{sc}$ have a small difference.

It is noteworthy that a high polymerization degree of the silica oligomers in the antisolvent could constrain the perovskite crystallization and consequently drop the photovoltaic properties of cells as it is apparent from inferior performance of cells with long stirring times of more than 10 min (Table 1). The efficiency of cells with 1 min stirring time (14.48%) was very close to the reference cells which indicates that a longer time is needed for noticeable hydrolysis and condensation reactions in solution as explained before. Furthermore, the photovoltaic performance of cells with 3 min stirring time (16.43%) was less than that of optimized cells with 2 min stirring time.

Concerning the energy levels in PS layers and in order to evaluate the origin of the improvement in photovoltaic properties of modified cells, steady-state photoluminescence measurements were conducted on pristine and modified PS layers. Figure 6a shows the PL spectra of the pristine and modified Cs$_{0.05}$ (MA$_{0.17}$ FA$_{0.83}$)$_{0.95}$ Pb (I$_{0.83}$ Br$_{0.17}$)$_3$ PS films. For both cells, the PL peak was located at 765 nm, while the PL intensity is markedly increased after modification. These results suggest a considerable drop in the density of trap states in the PS layers as nonradiative recombination centers while the bulk properties of the layer is unchanged as shown in Figures 1, 2, and 4.

The density of trap states was measured through the space-charge-limited current (SCLC) experiment (Figure 6b), which was carried out on the hole-only devices with ITO/NiO$_x$/perovskite/CIS/Au structure as presented at the inset of the figure.

Table 1. Photovoltaic Parameters of Cells: Photocurrent $J_{sc}$, Open Circuit Voltage $V_{oc}$, Fill Factor FF, and Efficiency PCE for Reference and Modified Cells as a Function of Stirring Time in TEOS Contained Antisolvents

| cell type          | $V_{oc}$(V) | $J_{sc}$(mA/cm$^2$) | FF (%) | PCE (%) |
|--------------------|-------------|---------------------|--------|---------|
| reference          | 1.03        | 22.32               | 62.49  | 14.36 ± 0.22 |
| M-Cell (1 min)     | 1.03        | 22.27               | 63.12  | 14.48 ± 0.13 |
| M-Cell (2 min)     | 1.03        | 22.78               | 71.25  | 16.72 ± 0.14 |
| M-Cell (3 min)     | 1.02        | 23.07               | 69.82  | 16.43 ± 0.09 |
| M-Cell (5 min)     | 1.02        | 22.81               | 68.62  | 15.96 ± 0.24 |
| M-Cell (10 min)    | 1.01        | 22.66               | 67.33  | 14.58 ± 0.11 |
| M-Cell (20 min)    | 1.01        | 21.83               | 64.03  | 14.26 ± 0.12 |
| M-Cell (30 min)    | 1.01        | 22.44               | 62.10  | 14.07 ± 0.15 |
| M-Cell (40 min)    | 1.04        | 22.72               | 59.69  | 14.10 ± 0.11 |
| M-Cell (50 min)    | 1.00        | 21.44               | 64.52  | 13.83 ± 0.17 |

Figure 7. (a) Nyquist plots of reference and modified cells. For both samples, two distinguishable arcs were observed at high and low frequencies, respectively. Nyquist plots were fitted by the equivalent circuit model presented in the inset of Figure 7. Here, $R_s$ is the series resistance, and $C_1$ and $R_1$ are associated with the high-frequency arc in the Nyquist plot. $C_2$ is the geometric capacitance of the perovskite in between the contact layers. $R_2$ corresponds to the conductivity of the perovskite layer and also can be affected by the transport resistance of the HTL.

$C_2$ and $R_2$ are related to the low-frequency arc of the Nyquist plot shown in Figure 7. $C_2$ originates from electronic and ionic charge accumulation at the electrode interfaces. $R_2$ is associated with the recombination at the perovskite interface with contacts.14 The fitting curves of the pristine and TEOS-modified cells are presented in Figure 7a also.
Regarding the same HTL layer in both structures, it is concluded that the bulk properties of the perovskite layer is preserved through the antisolvent modification.

On the other hand, devices with a modified antisolvent layer have higher $R_2$ values (156.06 $\Omega \cdot \text{cm}^2$) than pristine (76.95 $\Omega \cdot \text{cm}^2$) cells which explain the lower charge recombination at the interfaces of the perovskite layer and contacts. The lower recombination at interfaces led to improved fill factors in modified cells (Table 1).

In order to evaluate the capacitive processes in cells, the capacitance–frequency ($C$–$f$) plot of cells is presented in Figure 7b. According to the provided figure, modified cells, give a lower capacitance especially in mid-frequency ranges. The capacitive behavior in mid- and low-frequency ranges is attributed to the charge accumulation at interfaces as explained before.51

This proves the reduced interfacial charge accumulation at modified cells and consequently improved photovoltaic properties (Table 1). It is noticeable that the reduced interfacial charge accumulation in modified cells is in good agreement with considerably lower density of trap states (higher PL intensities) in modified perovskite layers as shown in Figure 6. In addition to the efficiency, by far the ambient stability is the most concerned subject in PS solar cells. In this context, the long-term stability of pristine and modified cells was explored under ambient conditions, relative humidity of 40 ± 2% and 27 ± 1 °C temperature (Figure 8). Receiving to near 20% of the initial efficiency after 290 h, pristine cells lost 80% of their initial performance. In the stark contrast, more than 85% of efficiency in TEOS-modified cells was achieved in the same time. Given stability results, reveals the effective passivation of perovskite layers by amorphous silica in modified cells.

3. CONCLUSIONS

Here, a simple modified antisolvent method was introduced for improving the performance of PSCs. According to our results the crystalline structure and the optical properties of the perovskite layer was preserved after modification while the surface trap states were decreased markedly. A considerable improvement in fill factors was obtained which is originated by the lower charge recombination in modified cells as confirmed by IS measurements. Furthermore, the long-term stability of cells under ambient conditions was noticeably improved in TEOS-modified cells. As a general conclusion, here a simple modified antisolvent method is introduced to deposit perovskite layers with superior properties for high-efficiency PSCs.

4. EXPERIMENTAL SECTION

4.1. Materials and Synthesizing Methods. Fluorine-doped tin oxide (FTO, Solaronix, 15 $\Omega$/square)-coated glass substrates were patterned with zinc powder and diluted hydrochloric acid. Provided substrates were successively cleaned by sonication in 2% Hellmanex water solution, deionized water, ethanol, acetone, and isopropanol for 10 min. After sintering at 450 °C for 15 min, UV-ozone treatment was performed to remove the possible residual contaminants. In order to deposit a TiO2 hole-blocking layer on FTO substrates, a 0.15 M TTIP (97% Merck, Germany) solution in ethanol was spin-coated at 2000 rpm, for 30 s and followed by sintering at 500 °C for 1 h. Afterward, a commercial TiO2 paste (IRASOL PST-20 T) diluted in ethanol (1:5.5 W ratio) and was spin-coated on the FTO/compact TiO2 layer at 4000 rpm for 30 s and annealed at 500 °C for 30 min. Before perovskite deposition, FTO/block-TiO2/meso-TiO2 substrates were treated with the UV-ozone for 5 min.

In order to prepare the perovskite precursor solution, PbI2 (1.1 M), FAI (1 M), MABr (0.2 M), CsI (0.05 M), and PbBr2 (0.22 M) were dissolved in anhydrous DMF: DMSO solvent (4:1 volume ratio). The Cs0.05 (MA0.17 FA0.83)0.95 Pb(I0.83 Br0.17)3 perovskite layer was coated on FTO/compact TiO2/...
mesoporous substrates through a two-step spin-coating at 1000 rpm for 10s and 4000 rpm for 20s, respectively. The chlorobenzene antisolvent was gently poured at the final 5 s of the second step. Also, some perovskite layers were prepared by utilizing a modified antisolvent material. Modified antisolvent was prepared by stirring chlorobenzene, TEOS, and deionized water with volume ratios of 2000, 15, and 3, respectively. The as-prepared perovskite layers were heated at 100 °C for 1 h. A thin layer of Spiro-OMeTAD hole-transport layer was spin-coated at 500 rpm for 30 s from a solution containing 72.3 mg Spiro-OMeTAD (99.5%, Borun Co, China) in 1 mL of chlorobenzene, 28.8 µL 4-tert-butylpyridin (Sigma-Aldrich), and 17.5 µL of a 1.8 M LiTFSI solution in acetonitrile. Finally, gold contacts (∼100 nm thickness) were thermally deposited to complete the devices.

4.2. Characterization Methods. X-ray diffraction patterns were acquired by XPert Pro MPD equipment with Cu Ka (λ = 1.54 Å) radiation. SEM micrographs were recorded using a MIRA3 TESCAN field-emission scanning electron microscope. Optical properties of the perovskite layers were taken with a PerkinElmer Lambda 25 spectrophotometer. The photocurrent—voltage measurements were performed under standard AM 1.5 (1000 W/m²) simulated light radiation by a Sharif solar SIM-1000 system (calibrated by a Thorlabs photodiode). The J–V curves were recorded by a Keithley 2400 digital SourceMeter while the cells were masked during the measurement with an active area of 0.09 cm². SCLC measurements were conducted on the hole-only devices with an ITO/NiOx/perovskite/CIS/Au architecture. NiOx and CIS layers were prepared according to the methods that we explained before.54,55 For the steady-state photoluminescence (PL) measurements, samples were excited by a 350 nm laser, and emissions were acquired by an AvaSpec 2048 TEC spectrophotometer. Electrochemical impedance spectroscopy (EIS) measurements were performed using Sharif Solar PGE-18 potentiostat/galvanostat in open circuit voltage and a frequency range between 1 Hz and 1 MHz with an AC amplitude of 20 mV. Extracted Nyquist plots from the EIS models in Zview software.

Author Information

Corresponding Authors
Mahmoud Samadpour — Department of Physics, K. N. Toosi University of Technology, Tehran 19679, Iran; orcid.org/0000-0003-2828-9195; Email: samadpour@kntu.ac.ir

Nima Taghavinia — Nanoparticles and Coating Lab, Department of Physics, Sharif University of Technology, Tehran 14588, Iran; Institute for Nano Science and Nanotechnology, Sharif University of Technology, Tehran 14588, Iran; orcid.org/0000-0001-6815-2041; Email: taghavinia@sharif.edu

Authors
Arezo Golchini — Department of Physics, K. N. Toosi University of Technology, Tehran 19679, Iran
Karim Abdizadeh — Material Science and Engineering Faculty, Sharif University of Technology, Tehran 14588, Iran
Mahsa Heydari — Nanoparticles and Coating Lab, Department of Physics, Sharif University of Technology, Tehran 14588, Iran
Mozhdeh Forouzandeh — Nanoparticles and Coating Lab, Department of Physics, Sharif University of Technology, Tehran 14588, Iran

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Tehran 14588, Iran; Department of Basic Sciences, Tarbiat Modares University, Tehran 17514115, Iran
Zahra Saki — Nanoparticles and Coating Lab, Department of Physics, Sharif University of Technology, Tehran 14588, Iran

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04058

Notes
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