Title:
The study of the morphology and structural, optical and J-V characterizations of (CH$_3$NH$_3$PbI$_3$) perovskite photovoltaic cells in ambient atmosphere.

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Abstract

In this paper, the synthesis processes of perovskite active films of CH$_3$NH$_3$PbI$_3$ have been studied for perovskite hybrid solar cells by spin and dip coating in ambient atmosphere, and without glove box to reduce production cost for technological applications. The morphology and structural, electrical and optical properties of perovskite films have been investigated by X-ray Diffraction (XRD), Field-Emission Scanning Electron Microscopes (FE-SEM), Atomic Force Microscopes (AFM) and Ultraviolet–visible spectroscopy (UV-Vis) and J-V curves measurements. A precursor solution of lead Iodide (PbI$_2$) with Dimethylformamide (DMF) solvent by spin coating at two stages (a) R=4500 rpm and (b) R=6000 rpm, and methyl ammonium iodide (CH$_3$NH$_3$I) with isopropanol solvent by dip coating have been prepared for active perovskite layer (CH$_3$NH$_3$PbI$_3$). The X-ray diffraction analysis approved the formation of (CH$_3$NH$_3$PbI$_3$) perovskite structure. The FE-SEM images of active layer (CH$_3$NH$_3$PbI$_3$) shown the formation of perovskite crystal structure as cubic crystalline beads which are in region of 20-30 nm. The UV-Vis optical absorbance analysis showed a band gap of 2.52 eV for PbI$_2$ film and 3.12 eV for CH$_3$NH$_3$I film. The J-V curves of hybrid solar cells have been characterized for R= 4500 and R=6000 rpm with efficiency of 2.40% and 4.65%, respectively.

Keywords: Perovskite solar cells, Methyl ammonium lead iodide, FE-SEM, CH$_3$NH$_3$PbI$_3$, Thin films.
1. Introduction

The polymer hybrid perovskite solar cells (PSCs) were introduced in 2009, and have been honored because of the rapid growth in the power conversion efficiency and flexible structure [1–5]. Perovskite solar cells as a new generation of solar cells with organic-mineral optical absorbents materials have attracted lots of researches due to their unique properties such as very high light absorption, excellent charge mobility, small exciton binding energy and low structural defects. The initial works in 2009, reported the efficiency of 3.81% for CH$_3$NH$_3$PbI$_3$/TiO$_2$, and open circuit voltage of 0.96 V for CH$_3$NH$_3$PbBr$_3$/TiO$_2$ solar cell. By technology advancements, optimization of parameters and replacement of absorbance materials with suitable energy gap, conversion efficiency has been increased considerably in recent years. The remarkable lab efficiency of 25.2 % in 2019 [6] for hybrid PbI$_2$ based perovskite solar cells was achieved by optimizing both resistance and band structure. Perovskite solar cells technology has entered its economic development phase and is beginning to explore the feasibility of various device designs and manufacturing processes for various applications. Companies are planning low-cost production lines, associating with silicon and CIGS solar cell manufacturers and attracting the interest of investors and savers. Detailed cost analysis of perovskite solar cell is not available except some comments about expected prices. The future years will be crucial for the upcoming of perovskite PV technology [7-16].

The organo-metallic halides as light absorbing layers of perovskite solar cells have higher conversion efficiency among low-cost materials. Thus, study of synthesis methods for active layer and their structural properties could have particular importance.

The regular formula for solar cell perovskite materials is MA (Pb, Sn) X$_3$. In this formulation, ‘X’ is a halogen ion such as I$^-$, Cl$^-$ and Br$^-$, M corresponds to CH$_3$ (methyl) and A is NH$_3$ (Ammonia). The methyl ammonium lead halide (CH$_3$NH$_3$ PbX$_3$) solar cells have high
temperature stability, low cost, surface passivation and more hardness in comparison with silicon based solar cells and offers a combination of excellent properties [17-21]. The perovskite based solar cells with activated layer of Methyl ammonium lead iodide (CH$_3$NH$_3$PbI$_3$) have been widely considered as a candidate for renewable energy applications and flexible solar cells. These layers have unique properties such as high carrier mobility, large absorption coefficient and high diffusion length of 1–3 μm [21,22] as light harvesting material. In the Methylammonium lead halides (CH$_3$NH$_3$PbI$_3$) crystal structure, the methylammonium cation (CH$_3$NH$_3^+$) is surrounded by PbI$_6$ octahedra (Figure 1). I$^-$ and NH$_3^+$ ions are not static and can drift through the crystal lattice with an activation energy of $E_a = 0.25$ and $0.60$ eV, respectively; and ion transportation is increased with structural holes [1, 3-5].

The methylammonium cations can rotate within their cages. At room temperature, ions have the CN axis aligned towards the face directions of the unit cells and the molecules randomly change to one of the six face directions on a 3 p seconds time scale [3-5].

The standard configuration of cell: FTO (Fluorine Tin Oxide) / TiO$_2$ /perovskite material (CH$_3$NH$_3$PbX$_3$) / cathode, has been introduced for planar heterojunction perovskite solar cells with a TiO$_2$ hole blocking layer. The TiO$_2$ as a porous layer and CH$_3$NH$_3$PbI$_3$ as active layer, are responsible parameters for efficiency in a perovskite solar cell. These layers directly play an important role in reducing the structural and electronic defects in the films which can affect the device performance and cell structure [23-25]. The crystal lattice of the methyl ammonium lead iodide (CH$_3$NH$_3$– PbI$_3$) perovskite have cubic or tetragonal structure (see Figure 1) [3-5].

On the other hand, a group of researchers have described in detail the chemical processes which lead to the degradation of perovskite material and their properties. They identified the five key factors of humidity, temperature, oxygen, ultraviolet radiation and heat, to have an important role in decomposition of perovskites [26].
Due to the sensitivity of perovskites to moisture during the manufacturing process and analysis of the solar cell device, the stability of the components is affected; and $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite decomposes to $\text{PbI}_2(S)+\text{CH}_3\text{NH}_3\text{I}$ ($aq$) and then HI. Decomposition of the compound usually begins at a moisture content of 55%, which can be seen by changing the color of the perovskite from dark brown to yellow. Also, the experiments showed that with increasing temperature to $T=56^\circ\text{C}$, perovskite tetragonal structure converts to cubic. Perovskite decomposition will significantly reduce the efficiency of the solar cell. However, with annealing the $\text{CH}_3\text{NH}_3\text{PbI}_3$ cell in Ar gas in glovebox, its stability is increased up to $T=120^\circ\text{C}$. Figure 2 shows humidity effects on degradation of cells parameters versus time [26, 27].

Preparation of titanium dioxide ($\text{TiO}_2$) blocking layer and $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite active layer is carried out by spin and dip coating methods. These layers, typically, are deposited using a one-step or two-step solution-processing method. However, it is difficult to control crystallinity and uniformity of films due to the annealing process, which is necessary for the one-step solution-processing method. In general, the two-step method offers better control of the perovskite morphology compared with the one-step method [23, 24]. However, $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film deposited by a dual-source of vacuum evaporation technique, has been developed for planar heterojunction perovskite solar cells, but this method requires advanced equipment. Therefore, the investigation of preparation methods with high-quality condensed layer and easy control of fabrication processes is very important [26-30].

In this work, a step by step and simple method for the synthesis of hybrid perovskite solar cell layers with structure of $\text{Au/FTO (anode)/TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Au (cathode)}$ has been presented, and optimized conditions for optical active perovskite layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ ($\text{MAPbI}_3$) by spin and dip coating have been reached. The environmental efficiency of cells for general applications and possibility of their expansion was evaluated. All steps of
processing layers carried out in free environment and without the glove box due to achieve a low cost- process for technological aims. Then, structural, optical and electrical properties of layers such as crystalline structure, surface morphology, transmittance and energy band gap were investigated by XRD, FE-SEM, AFM and UV-Vis spectroscopy. Also, The J-V cure of the fabricated hybrid solar cells have been characterized.

2. Experimental details

2.1. Materials

Fluorine-doped tin oxide (FTO) coated glasses, Titanium dioxide (TiO₂) hole blocking layer, PbI₂ (Sigma-Aldrich, powder), Methylamine-Iodide (CH₃NH₃I), N’N-Dimethylformamide (C₃H₇NO) (Sun lab group) as solvent for PbI₂, 2-Propanol (CH₃CH (OH) CH₃; C₃H₈O) (Merck Company) as solvents for CH₃NH₃I.

2.2. Processing of perovskite active layer with TiO₂ blocking layer

Fluorine-doped tin oxide (FTO) coated glasses were cleaned in an ultrasonic bath once in deionized water (20 min) and subsequently twice in ethanol and acetone (20 min each). Deposition of layers was carried out in following stages according to Figure 3.

(a)-Removing FTO layer:

As seen in Figure 4, FTO was removed from the anode contact, to prevent shunting upon contact with measurement pins, by etching the FTO with 2 M HCl (Merck) and Zinc powder (V. Gene Par Delta Co.). Substrates were cleaned as above again and then annealed at 120 °C for 10 min, resulting in the formation of a transparent film [25].

(b)- TiO₂ coating:

A solution of titanium isopropoxide (Merck) in absolute ethanol (430 mM) (Merck) and 27 mM solution of HCl in ethanol were mixed together slowly. This solution was spin coated at 2000 rpm for 30 s to make a TiO₂ blocking layer. The compact layer was then sintered at 100 °C for 30 min and 500 °C for 30 min.
(c) PbI$_2$ coating:

After cooling to room temperature, preparing the perovskite active layer (CH$_3$NH$_3$PbI$_3$) by two-step spin-dip coating methods was carried out.

In the first step; PbI$_2$ solution (1 M) was prepared by dissolving 462 mg of PbI$_2$ in 1 ml Dimethyl-formamide (DMF) under stirring at 70 °C for overnight. PbI$_2$ solution was deposited by spin coating for $t = 5$ s and at: (a) $R=4500$ rpm and (b) $R= 6000$ rpm. After spinning, the film was dried at 40 °C for 3 min and 100 °C for 5 min.

(d) Optical absorption coating: Perovskite film (CH$_3$NH$_3$PbI$_3$)

In the second step; methyl ammonium iodide (CH$_3$NH$_3$I) solution was prepared by dissolving 9 mg CH$_3$NH$_3$I in 1 ml isopropanol (IPA) under stirring at the room temperature for three hours (see Figure 5). The methyl ammonium iodide (CH$_3$NH$_3$I) poly-crystal layer was coated on lead iodide layer through deep coating in a solution of CH$_3$NH$_3$I+ isopropanol with spin coating in 2000 rpm to form a uniform layer. The sample was kept on the hot plate at 100°C for 5 min to form crystalline perovskite (CH$_3$NH$_3$PbI$_3$) film [26].

3. Characterizations

The samples were characterized by X-ray diffraction (XRD) by D8 Advance Bruker system with Ni filter using Cu Ka ($\lambda = 0.15406$ nm) radiation. Field emission scanning electron microscopy (FE-SEM), TESCAN company, model: MIRA$_3$, was used for studying the surface properties. The optical measurements carried out using Unico 4802 double-beam UV–Vis spectrophotometer system in the range of 190–1100 nm. The morphological properties were studied with atomic force microscopy (AFM) performed by DME system: Model: Igloo-95-50E. The electrical properties of layers were studied by Ecopia HMS-7000 Photonic Hall Effect Measurement System. Solar simulator system, by Nanosat Co, with light intensity of 1000 mW/cm$^2$ was used for testing solar cell samples.
4. Results and Discussion

4.1. Structural properties

The X-ray Diffraction (XRD) analysis has been performed, in order to confirm the formation of TiO$_2$/FTO and CH$_3$NH$_3$PbI$_3$ perovskite structure for each of the single layers. The structural characterization of coatings and their results have been shown in Figures 6(a) to 6(d).

Figure 5(a) shows TiO$_2$/FTO oxide films with basic peaks of F-doped SnO$_2$ and TiO$_2$ and an amorphous background. Figures 6(b), 6(c), and 6(d) show XRD patterns of PbI$_2$/FTO, CH$_3$NH$_3$PbI$_3$/FTO and CH$_3$NH$_3$PbI$_3$/TiO$_2$/FTO samples, respectively. The results for both samples clearly showed that the characteristic peaks of perovskite are present in the XRD patterns in Figures 6(c) and 6(d). In agreement with other reports [27], the peaks at the diffraction angles of 14.7°, 28.5°, 41.2° and 43.06° are assigned to the planes of (110), (220), (224) and (314) of the perovskite structure. This result indicates proper conversion of PbI$_2$ into the perovskite structure in all CH$_3$NH$_3$I concentrations. However, separate peaks of lead iodide (PbI$_2$) are also seen in samples, which indicates a failure to complete the Perovskite reaction. It should be noted that recent research shows that a residual of pure lead iodide is remained. In the structure of perovskite, lead iodide can have a positive role in standard single-halogen cells or multiple halogens [24, 25]. To compare the structure and morphology of the samples, FE-SEM images (up-left and up-right) in figures 5(b) and 5(d) have been brought and they will be discussed in next section.

4.2. Morphology of PbI$_2$ and CH$_3$NH$_3$PbI$_3$ / TiO$_2$ / FTO Layers by FE-SEM

The surface morphology of the PbI$_2$/ TiO$_2$ / FTO layers by spin coating in R= 4500 rpm/min were studied using field emission scanning electron microscope (FE-SEM) images which are shown in Figures 7 (a) to (c) with magnifications of 50 KX, 100 KX and 200KX, respectively.
As indicated in Figure 7(a), the iodide layers (PbI₂) deposited by spin coating in R=4500 rpm have a regular branch structure and/while the TiO₂ has nanoparticle structure. From Figures 7(b) and 7(c), the diameter of the branches is measured in range of 500 to 700 nm and the size of nanoparticles in the range of 50-100 nm.

Figures 8(a) to 8(d) show FE-SEM images of CH₃NH₃PbI₃ / TiO₂ / FTO sample in R=4500 rpm after coating the methyl ammonium iodide layer (CH₃NH₃I) by dip coating method on the substrate /FTO/titanium dioxide /PbI₂. As indicated in the Figure 8(a) and 8(b), the perovskite crystals are observed as well-formed cubic crystalline beads, placed on branch-like framework. Form Figures 8(c) and 8(d) and, the diameter of the cubic crystalline beads is in range of 200 to 300 nm. However, there are also empty spaces or holes due to the presence of vacant spots in the lead iodide layer [27].

As indicated in Figure 9(a), the iodide layers (PbI₂) deposited by spin coating in R=6000 rpm have a regular leaf-like morphology while the TiO₂ has nanoparticle structure. As seen in Figures 9(b) and 9(c), the diameter of the leaves is observed in range of 50 to 80 nm and the size of TiO₂ nanoparticles is in the range of 5-10 nm.

Figures 10(a) to 10(d) show FE-SEM images of CH₃NH₃PbI₃ / TiO₂ / FTO sample after placing the methyl ammonium iodide layer (CH₃NH₃I) deposited by dip coating method with R=6000 rpm on the substrate PbI₂/ titanium dioxide /FTO. As indicated in the Figures 10(a) and 10(b), the perovskite crystals are observed as well-formed cubic crystalline beads, placed on grain-like framework. From Figures 10 (c) and 10 (d), the size of the cubic crystalline beads is in range of 50 to 70 nm. This morphology is in agreement with other literatures, there are also empty spaces or holes due to the presence of vacant spots in the lead iodide layer [27-28]. Thus, images of the FE-SEM of the lead iodide layer presented the structure of branch-like for R=4500 rpm and regular leaves-like and uniform for R= 6000 rpm which had better morphology.
4.3. Atomic Force Microscopy (AFM) images

The atomic force microscopy (AFM) images from the surface of TiO$_2$ on FTO and the surface of the perovskite layer CH$_3$NH$_3$PbI$_3$ are shown in figures 11(a) to 11(c). As seen in figure 11(b), a uniform distribution of the Perovskite crystals is formed. The particles size is nearly uniform and the largest size is ~60 nm. Figure 11 (c) shows a granular and rather inhomogeneous MAPbI$_3$ topography with a film thickness of 0.5 µm and a large amount of surface areas, which is ideal for the study of the degradation process.

4.4. Optical band gap

To determine the optical band gap in the hybrid halide perovskite, we measured the transparency and absorption spectra for two solvents of lead iodide (PbI$_2$) with DMF and methyl ammonium iodide (CH$_3$NH$_3$I) with IPA by UV–Vis spectroscopy, as shown in Figure 11. The optical band gap values of crystalline materials can be calculated with plots of $(\alpha h \nu)^2$ vs $h \nu$ using the Davis and Mott equation by [28]:

$$ (\alpha h \nu) = A^+ (h \nu - E_g)^m $$  \hspace{1cm} (1)

In this relation, $A^+$ is a constant, which does not depend on photon energy and $E_g$ is the optical band-gap energy and $m$ is an exponent that indicates the type of the optical transmittance (direct or indirect) and the structure feature of the material (crystalline or amorphous) [29]. Table 1 show the values of band gap and particles size for solar cell layers. Figure 12(a), shows a band gap of 2.52 eV for the pure PbI$_2$ solvent, consistent with the yellow color solution PbI$_2$ and DMF. As shown in Figure 12(b), The CH$_3$NH$_3$I solvent shows a band gap of 3.12 eV, consistent with the solution CH$_3$NH$_3$I and IPA (Isopropanol). Figure 12 (c) presents band gap of 1.92 eV for CH$_3$NH$_3$PbI$_3$ perovskite layer after deposition of PbI$_2$ + CH$_3$NH$_3$I compound films. These values match the previous reports [24].
4.5. Hall Effect measurement

In solid state physics, Hall Effect experiment is an important tool for electrical characterization of the materials, especially semiconductors. It directly determines both the sign and density of charge carriers in a given sample. If electrical charge carriers of the conductor placed in a perpendicular (B) magnetic field, a vertical potential difference ($V_H$) will be generated in the two edges of conductor which is perpendicular to both magnetic field and current. This phenomenon is called Hall Effect. The Hall Effect measurement carried out for CH$_3$NH$_3$PbI$_3$ perovskite layer and value of $R_S$ and mobility ($\mu$) of the layers for R= 4500 rpm and R=6000 rpm is given in Table 2.

4.6. I-V characterize

I-V diagram of solar cell with structure of FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/Au, and output parameters under solar simulator system are shown in Figure 13 and Table 3. The fill factor (FF%) and efficiency ($\eta$) of solar cells obtained from relations 2 and 3 [31].

\[
FF = \frac{P_m}{P_n} = \frac{V_m \times J_m}{V_{oc} \times J_{sc}} \quad (2)
\]

\[
\eta (\%) = \frac{P_{out}}{P_{in}} = \frac{FF \times V_{oc} \times J_{sc} \times 100}{P_{in}} \quad (3)
\]

In this relation, $V_{oc}$ is open-circuit voltage and $I_{sc}$ is short-circuit current.

Perovskite structure in this work is a common structure in organic solar cells but all the steps in synthesis of the layer are done in a way to be low cost. Materials used in this layer do not have high purity content to reduce costs as much as possible. In addition, the cell made in this study is synthesized without a hole transfer layer and we can conclude with these normal conditions, the fill factor (68.0%) and efficiency (4.65%) of solar cell (Figure 13(a)) is suitable for industrial applications. As seen from Figure 13 (a') and 13(b'), efficiency of sample with R= 6000 is higher and it is related to morphology type and grain boundary and also carrier mobility ($\mu$) of films.
5. Conclusion

In this paper, the CH$_3$NH$_3$PbI$_3$ perovskite absorbing layer was prepared with integrations of the porous titanium dioxide as electron transfer layer. The microstructure and optical properties of CH$_3$NH$_3$PbI$_3$ perovskite thin films have been investigated by two steps with spin coating at two stages (a): R=4500 rpm and (b): R= 6000 rpm. The effect of the layers on each other in formation of the crystalline structure was studied.

The importance of this method due to industrial purposes and low-cost processes is:

(a) deposition of all the addressed layers in ambient atmosphere,
(b) having normal deposition conditions without the glove box, annealing or vacuum,
(c) cheap raw material and
(d) good quality and excellent morphology of layers and uniform formation of the active crystalline layer.

The X-ray diffraction analysis (XRD) was carried out for all layers and the formation of crystalline structure of the samples was studied. The XRD analysis approved the formation of perovskite crystal structures with characteristic peaks corresponding to the planes of (110), (220), (224) and (314).

The electron microscope images (FE-SEM) of the lead iodide layer presented the structure of branch-like for R=4500 rpm and regular leaves-like and uniform for R= 6000 rpm which had better morphology. The images taken from the perovskite layer confirmed the crystalline structure of the perovskite which crystals are formed as cubic crystalline beads in the nanoscale.

The morphology of the perovskite layer by AFM showed a homogeneous topography of MAPbI$_3$ with a thickness of ~0.5 µm and a large surface area, which is ideal for the study of the surface processes. The optical absorbance analysis by UV-Vis spectroscopy showed a band gap of 2.52eV for PbI$_2$ and 3.12 eV for CH$_3$NH$_3$I. Using the Hall Effect measurement, in the perovskite layer, the conductivity (σ) of active layer is equal to 1.28×10$^3$ Ω$^{-1}$.cm$^{-1}$ with
absorbance coefficient of ($\alpha$) $10^5$ cm$^{-1}$. The efficiency 4.65% of sample with R= 6000 rpm is higher and is related to morphology type, grain boundary and mobility ($\mu$) of films. Due to the fact that materials and equipment used in this work are cheap and available, this method can be practical, and reliable for commercial applications.

**Reference**


Biographies:

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Mehdi Adelifard received his PhD degree in Condensed Matter Physics from Shahrood University of Technology in 2012. He is associated Professor in the School of Physics at Damghan University. His research is situated in the field of Technology & Innovation, with a special focus on thin films solar cells, synthesis of nanostructured materials, and cellulose and carbon aerogels for environmental applications. He has published more than 35 journal papers.
**Figures Captions:**

**Figure 1:** Crystal lattice of the methyl ammonium lead iodide (CH$_3$NH$_3$-PbI$_3$) perovskite structure: (a): Cubic, (b) Tetragonal and (c): Mobile ions [3-5].

**Figure 2:** Degradation and humidity effect on cells parameters versus time (days) [26].

**Figure 3:** Flowchart of synthesis process for the CH$_3$NH$_3$PbI$_3$ perovskite layer.

**Figure 4:** Schematic view of etching process on FTO/Glass.

**Figure 5:** Scheme that illustrates the deposition of the CH$_3$NH$_3$PbI$_3$ perovskite via sequential deposition techniques. PbI$_2$ is first deposited via spin-coating and then subsequently CH$_3$NH$_3$I solution deposited via dip coating and it transformed into CH$_3$NH$_3$PbI$_3$ by annealing processes at T= 100°C, (b) PbI$_2$ layer and (c) CH$_3$NH$_3$PbI$_3$ perovskite layer.

**Figure 6:** The XRD patterns of samples (a) Glass/FTO/TiO$_2$, (b) Glass/FTO/PbI$_2$, (c) Glass/FTO/CH$_3$NH$_3$PbI$_3$ and (d) Glass/FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$, and SEM images from morphology samples with R=4500 (up-left) and R=6000 (up-right).

**Figure 7:** The SEM images of Glass/FTO/TiO$_2$ (block layer)/PbI$_2$ thin film for R= 4500 rpm/min: (a) 25 KX, (b) 50 KX and (c) 100 KX.

**Figure 8:** The SEM images of the surface morphology of a Glass/FTO/TiO$_2$ (block layer)/MAPbI$_3$ thin film for R= 4500 rpm: (a) 25 KX, (b) =50 KX and (c): 100 KX.

**Figure 9:** The SEM images of Glass/FTO/TiO$_2$ (block layer)/PbI$_2$ (a)=25 KX, (b)=50 KX, and (c) =100KX, for R= 6000 rpm.

**Figure 10:** The SEM images of the surface morphology of a Glass/FTO/TiO$_2$ (block layer)/MAPbI$_3$ thin film, for R= 6000 rpm (a): 25 KX, (b) 50 KX and (c): 100 KX.

**Figure 11:** AFM images from surface of (a) TiO$_2$ on FTO, (b) Perovskite layer CH$_3$NH$_3$PbI$_3$ and (c) distribution highest of layer CH$_3$NH$_3$PbI$_3$. 
Figure 12: Plot of $(\alpha \nu)^2$ vs $\nu$ for (a) Lead Iodide (PbI$_2$) film, (b) Methyl Ammonium Iodide (CH$_3$NH$_3$I) film and (c) CH$_3$NH$_3$PbI$_3$ film for $R=6000$ rpm.

Figure 13: J-V curves of the perovskite solar cells with Au/FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/Au structure for (a) $R=6000$ rpm and (b) $R=4500$ rpm and image of the samples with Au-electrodes (above), and EE-SEM graphics from morphology and grain boundary of films: (a’) $R=6000$ rpm and (b’) $R=4500$ rpm.
Table 1: Physical parameters of cell layers.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Particle size (nm) by FE-SEM</th>
<th>Band gap (eV)</th>
<th>Thickness layer (nm) by FE-SEM</th>
<th>Transparency (λ in 650 nm)</th>
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</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}</td>
<td>~50</td>
<td>3.27</td>
<td>~100</td>
<td>~92</td>
</tr>
<tr>
<td>PbI\textsubscript{2}</td>
<td>~60</td>
<td>2.52</td>
<td>~220</td>
<td>~26</td>
</tr>
<tr>
<td>CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}</td>
<td>~80</td>
<td>1.92</td>
<td>~448</td>
<td>~45</td>
</tr>
</tbody>
</table>

Table 2: Hall effect measurement of active layer (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}) for R= 4500 and 6000 rpm.

<table>
<thead>
<tr>
<th>Rate of spinning (rpm)</th>
<th>Sheet Resistance (R\textsubscript{s}) (Ω/sq)</th>
<th>Conductivity (σ) (1/Ω.cm)</th>
<th>Mobility (µ) (cm\textsuperscript{2}/Vs)</th>
<th>Average Hall Coefficient (R\textsubscript{H}) (cm\textsuperscript{3}/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=6000</td>
<td>11.3</td>
<td>1.28\times10\textsuperscript{3}</td>
<td>21.1</td>
<td>- 1.64\times10\textsuperscript{-2}</td>
</tr>
<tr>
<td>R=4500</td>
<td>11.7</td>
<td>1.24\times10\textsuperscript{3}</td>
<td>8.6</td>
<td>-6.93\times10\textsuperscript{-3}</td>
</tr>
</tbody>
</table>

Table 3. Output parameters of solar simulator system for FTO/TiO\textsubscript{2}/ CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/Au solar cell device at R= 4500 and 6000 rpm.

<table>
<thead>
<tr>
<th>Rate of spinning (rpm)</th>
<th>J\textsubscript{SC} (mA)</th>
<th>J\textsubscript{m} (mA)</th>
<th>V\textsubscript{m} (V)</th>
<th>V\textsubscript{OC} (V)</th>
<th>FF</th>
<th>Efficiency (η) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=6000</td>
<td>0.38</td>
<td>0.31</td>
<td>0.150</td>
<td>0.185</td>
<td>0.68</td>
<td>4.65</td>
</tr>
<tr>
<td>R=4500</td>
<td>0.35</td>
<td>0.22</td>
<td>0.110</td>
<td>0.180</td>
<td>0.38</td>
<td>2.40</td>
</tr>
</tbody>
</table>
Figure 1: (a), (b) and (c) [3-5].
Figure 2 [26].
Figure 3: Flowchart of coating process.

1. Etching the FTO with 2M of HCl and Zinc powder.

2. Cleaning FTO coated substrate layer in an ultrasonic bath once in deionized water (20 min) and subsequently twice in ethanol and acetone (20 min) and annealing at T=120 °C (10 min).

3. Coating of TiO₂ blocking layer by spin coating (2000 rpm in t =30s)
   - Annealing at T=100 °C (30 min) and then T=500 °C (30 min)

4. Spin Coating PbI₂ + DMF solution by two step of spin coating:
   - (a) R=4500 rpm at t = 5 s and
   - (b): R=6000 rpm at t =5 s

5. Dip Coating CH₃NH₃I solution (CH₃NH₃I + Isopropanol) at t=20 s

6. PbI₂ on CH₃NH₃I layer,
   - Annealing at T=100°C (5 min)

7. Formation of CH₃NH₃PbI₃ Perovskite layer
Figure 4.
Figure 5: (a), (b) and (c).
Figure 6: (a), (b), (c) and (d).
(a) FTO+TiO$_2$+PbI$_2$

(b) FTO+TiO$_2$+PbI$_2$
Figure 7: (a), (b), and (c).

(c) FTO+TiO$_2$+PbI$_2$
(a) FTO+TiO$_2$+CH$_3$NH$_3$PbI$_3$

(b) FTO+TiO$_2$+CH$_3$NH$_3$PbI$_3$
Figure 8: (a), (b), (c) and (d).

(c) FTO+TiO$_2$+CH$_3$NH$_3$PbI$_3$

(d) FTO+TiO$_2$+CH$_3$NH$_3$PbI$_3$
(a) FTO+TiO₂+PbI₂

(b) FTO+TiO₂+PbI₂
(c) FTO+TiO\textsubscript{2}+PbI\textsubscript{2}

Figure 9: (a), (b), and (c).
(a) FTO+TiO$_2$+CH$_3$NH$_3$PbI$_3$

(b) FTO+TiO$_2$+CH$_3$NH$_3$PbI$_3$
Figure 10: (a), (b) (c) and (d).

(c) FTO+TiO$_2$+CH$_3$NH$_3$PbI$_3$

(d) FTO+TiO$_2$+CH$_3$NH$_3$PbI$_3$
Figure 11: (a), (b), (c).
(a) - PbI$_2$

(b) - CH$_3$NH$_3$I
Figure 12: Plot of $(\alpha h \nu)^2$ vs $h \nu$ for (a) - Lead Iodide (PbI$_2$) film, (b) - Methyl Ammonium Iodide (CH$_3$NH$_3$I) film and (c): CH$_3$NH$_3$PbI$_3$ film for R=6000 rpm.
Figure 13: J-V curves of the perovskite solar cells with Au/FTO/TiO₂/CH₃NH₃PbI₃/Au structure for (a) R=6000 rpm and (b) 4500 rpm and image of the samples with Au-electrodes (above), and EE-SEM graphics from morphology and grain boundary of films: (a') R=6000 rpm and (b') R=4500 rpm.