

Perovskite/polymer solar cells prepared using solution process

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Abstract. We report a simple solution-based process to fabricate a perovskite/polymer tandem solar cell using inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$ as an absorber and organic PCBM (6,6 phenyl C61-butyric acid methyl ester) as an electron transport layer. The absorber solution was prepared by mixing the $\text{CH}_3\text{NH}_3\text{I}$ (methyl ammonium iodide) with PbI_2 (lead iodide) in DMF (N,N-dimethyl formamide) solvent. The absorber and electron transport layer were deposited by spin coating method. The electrical characteristics generated from the cell under 50 mW/cm^2 at 25°C comprised of an open circuit voltage of 0.31 V , a short circuit current density of 2.53 mA/cm^2 , and a power conversion efficiency of 0.42% .

1. Introduction

In recent years, novel research in the field of halide perovskites nano crystals have drawn much attention as a new class of light absorber layers for solar cells [1]. The perovskites exhibit a semiconductor-to-metal transition with the increase in the dimensionality [2,3]. By increasing the dimension from 2D to 3D, the band gap will be decreased and the electrical properties will change [2]. Solar cells based on perovskite materials were first reported in 2009 by Miyazaka et.al. They applied 3D organometallic halide perovskites in a liquid electrolyte configuration dye-sensitized solar cell (DSSC) with a power conversion efficiency (PCE) of 3.8% [3,4].

The general formula of organometallic halide perovskites is $\text{CH}_3\text{NH}_3\text{PbX}_3$, where X can be Cl, Br, or I. Perovskite is basically a semiconductor that offers a wide range of band gap tuning by modifying the halide content and the organic part [5]. Methyl ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) was initially utilized as a sensitizer, in the form of nanoparticles decorating the surface of a mesoporous metal oxide, in a liquid-state dye-sensitized solar cells[6]. $\text{CH}_3\text{NH}_3\text{PbI}_3$ has a band gap of 1.55 eV , close to the theoretical bandgap for an optimum photovoltaic performance (i.e. 1.4 eV) [7]. This coupled with a good extinction coefficient, which is one order of magnitude higher than standard dyes, enables excellent external quantum efficiency spectra (EQE) in the solar cells. This corresponds to an optimum photon absorption in the visible range (400 to 800 nm) and part of the near-infrared of the solar spectrum. Furthermore, when $\text{CH}_3\text{NH}_3\text{PbI}_3$ is heated above $55\text{--}60^\circ\text{C}$, it undergoes a phase transition from tetragonal to cubic, which is expected to narrow the band gap of the material [7].

The great deal of interest and research activities involving perovskite solar cells have resulted in a tremendous progress in the PCE, with more than 17% of improvement was attained within a very short time scale [8]. However, the breakthroughs have been mostly achieved in a dye-sensitized solar cell



architecture that typically requires high-temperature processing due to the use of metal oxides as the charge transporting materials [8]. As an alternative, organic photovoltaic (OPV) structure has gained much consideration as it can be fabricated through simple and low-temperature processing, including being adaptable for flexible photovoltaic applications [4,8]. The combination of a perovskite and OPV concept therefore holds a great potential and deserves further studies.

Herein, we report the fabrication of perovskite/polymer solar cells using $\text{CH}_3\text{NH}_3\text{PbI}_3$ as an absorber and PCBM (6,6 phenyl C61-butyric acid methyl ester) as an electron transport layer. The device comprised of a glass/ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Ag, wherein the perovskite and polymer layer were deposited by spin coating. Spin-coating is a well-known, rapid technique used for producing uniform, high-quality thin films on various substrates. This coating method has been widely used in the fabrication of organic electronics and optical device coatings, among many others [4]. In this research, we prepared a thin film of the low temperature solution-processed organometallic trihalide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) absorber by mixing $\text{CH}_3\text{NH}_3\text{I}$ (methyl ammonium iodide) with PbI_2 (lead iodide) in DMF (N,N-dimethyl formamide) solvent. The performance of the solar cell was subsequently evaluated by calculating the power conversion efficiency under solar simulator.

2. Methodology

All chemicals in this work were commercially available and used without further purification. The substrate used was 12.5 mm \times 12.5 mm indium tin oxide (ITO) coated glass with a sheet resistance of 12 Ω /square. ITO is a transparent conductive oxide that serves to drain the photogenerated holes. To avoid any short circuit on the cell, it is therefore necessary to form an ITO pattern by partially etching the ITO layer. A black paint was sprayed on the ITO surface that has been covered with an adhesive tape mask with a certain pattern. The substrate was then dried at room temperature overnight, and the mask was then removed once it dried. The next step was the etching process, aiming at eliminating the undesired ITO layer. Etching process was performed by dipping the substrate into 50% HCl solution for 5 minutes, followed by washing in DI water and drying at room temperature. The remaining paint was then removed by consecutively immersing the substrate into tinner solution, isopropyl alcohol, and DI water for 10 min each in an ultrasonic bath.

The next step was the coating of the hole transporting layer, which was made of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). PEDOT:PSS coating was carried out using spin coating method at a rotation speed of 1000 rpm for 60 s. The PEDOT:PSS layer was then dried in a vacuum oven at 120 $^\circ\text{C}$ for 60 min.

The organometallic halide perovskites were then prepared by mixing $\text{CH}_3\text{NH}_3\text{I}$ with PbI_2 (molar ratio 1:1) in 1 mL DMF. The solution was stirred at room temperature for 24 h. The solution mixture was subsequently spin coated on top of the PEDOT: PSS layer at 2500 rpm for 30 s and then annealed in a vacuum oven at 100 $^\circ\text{C}$ for 45 minutes.

The polymer solution was prepared by dissolving 20 mg PCBM in 1 mL chlorobenzene and stirred for 60 s. The PCBM solution was then deposited onto the perovskite layer by spin coating at 1000 rpm for 30 s, and annealed in a vacuum oven at 100 $^\circ\text{C}$ for 10 min. Finally, a 60 nm-thick silver electrode was deposited by thermal evaporation onto the polymer layer. The size of the active area of each cell was 5.0 mm \times 6.0 mm. Characterization

The ultraviolet–visible (UV-vis) absorption spectra of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer were recorded using UV-vis spectrophotometer (Hewlett Packard 8453 Agilent Technologies). The surface morphology of the samples was observed using a scanning electron microscopy (SEM) in an FEI Quanta 250. The photovoltaic performance of solar cells was measured under solar simulator comprising of a Xenon lamp (Oriel, Newport, USA, AM 1.5) and a National Instrument source meter, which was integrated to a Lab-view software. The irradiation intensity was set to 50 mW/cm² at 25 $^\circ\text{C}$.

3. Results and Discussion

The basic device configuration of the fabricated perovskite/polymer tandem solar cell is illustrated in Fig. 1, which consists of ITO coated glass substrate deposited consecutively with PEDOT:PSS as the

hole transport material, $\text{CH}_3\text{NH}_3\text{PbI}_3$ as the absorber, PCBM as electron transport material, and finally Ag metal layer as the electrode. Such structure is so called an inverted perovskite architecture, as the electron and hole transporting layer are the opposite of those used in the inorganic-based perovskite solar cells. The crystal structure of the organometal halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the molecular structure of the PCBM is shown in Fig. 2a and 2b, respectively.

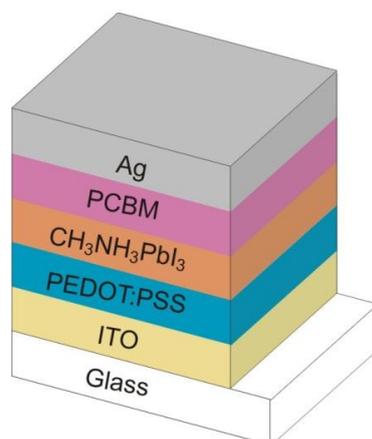


Figure 1. Device configuration of perovskite/polymer solar cells comprising of $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM layer.

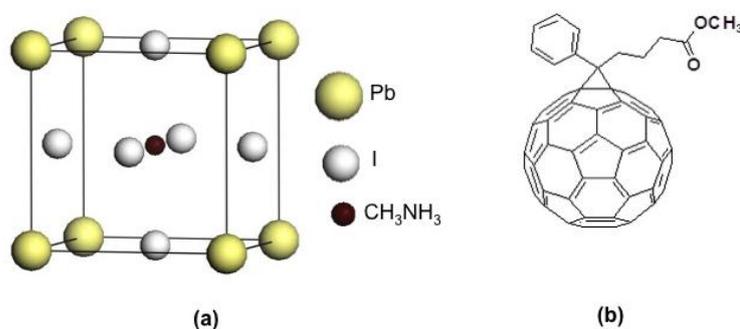


Figure 2. (a) Crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and (b) molecular structure of PCBM.

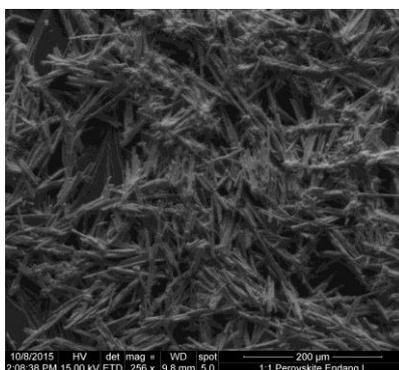


Figure 3. SEM image of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface layer at $\times 256$ magnification.

Fig. 3 shows the SEM image of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface layer at $\times 256$ magnification. An irregular dendrite-like shape with a length in the range of hundreds of micrometers was formed on top of the substrate. There were some areas that were not fully covered by the dendrite layers, indicating that the perovskite layer was non-uniform and uneven. The low surface coverage with some uncoated areas could lead to light penetrating through the surface layer and, therefore reducing the light absorption. This phenomenon was similar to the report from Salim et al. [8]. They reported that one of the main challenges to obtain good performance in planar perovskite devices is the fabrication of high quality films with controlled morphology, high surface coverage and minimum pinholes [8].

The UV-vis absorption spectrum of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer prepared from the mixture of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 precursor is shown in Fig. 4. It can be seen that the perovskite layer exhibited a narrow range of optical absorption from 300 to 440 nm. The first peak absorption with the highest absorption intensity of 0.80 a.u. was located at 320 nm. The second peak was located at ~ 410 nm with an intensity of 0.65 a.u. This optical profile indicates that the perovskite layer tends to absorb ultraviolet light more than the blue light. Using the transformed Kubelka-Munk function, $(\alpha h\nu)^2$ vs. $h\nu$, for a direct semiconductor [9], the bandgap energy for the obtained $\text{CH}_3\text{NH}_3\text{PbI}_3$ was estimated to be ~ 2.8 eV.

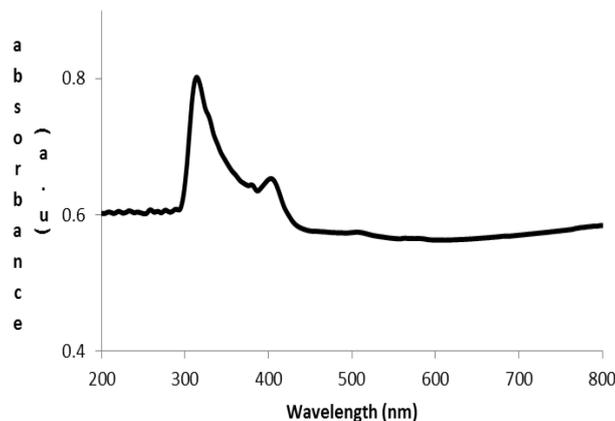


Figure 4. Absorption spectrum of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer prepared from the precursor solution of the mixed $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 .

The photovoltaic performance of the perovskite/polymer solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ was characterized under illumination of 50 mW/cm^2 . The J-V curve and the corresponding electrical parameters are presented in Fig. 5 and Table 1, respectively. As seen in Table 1, an open circuit voltage (V_{oc}) of 0.31 V and a short circuit current density (J_{sc}) of 2.53 mA/cm^2 were obtained, resulting in a power conversion efficiency of 0.42%. The values of these parameters were lower compared to the reported values in the literature [10]. By using same cell configuration with this experiment, Jeng et al. for example, found greater values for all of the electrical characteristic parameters, with V_{oc} , J_{sc} , FF, PCE, R_s , and R_{sh} reached 0.60 V, 10.32 mA/cm^2 , 0.63, 3.90%, $1.82 \Omega \text{ cm}^2$, and $3930 \text{ k}\Omega$, respectively [10].

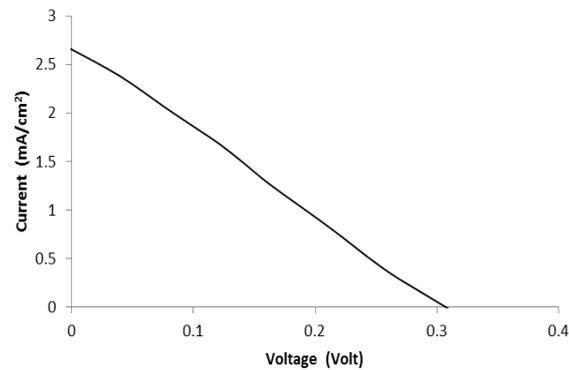


Figure 5. J - V curve of the perovskite/polymer solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ under solar illumination with an intensity of 50 mW/cm^2 .

Table 1. Electrical Characteristics of the perovskite/polymer solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ under illumination with an intensity of 50 mW/cm^2 .

V_{oc} (volt)	J_{sc} (mA/cm^2)	Fill factor	R_{seri} ($\Omega \text{ cm}^2$)	R_{shunt} ($\text{k}\Omega$)	PCE (%)
0.31	2.53	0.27	132.70	0.47	0.42

There are several factors that could be the reason for the poor performance exhibited by the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ tandem solar cell fabricated in this work. It can be observed in in Fig. 4 that the J - V curve formed a relatively linear line, which was far from the ideal square-shape curve. This corresponded to a low fill factor value ($\text{FF} = 0.27$), which was the result of a high series resistance ($R_s = 132.7 \Omega \text{ cm}^2$) and low parallel or shunt resistance ($R_{sh} = 0.47 \text{ k}\Omega$). The high R_s could be linked to the thickness of each active layer and the bad contact between the cathode and anode layer in the cell. The high R_s and the low R_{sh} could also contribute to the low J_{sc} . The low J_{sc} might be mainly caused by the thickness of perovskite layer, which was allegedly greater than the charge carrier diffusion length [11]. When the perovskite layer is too thick, the photogenerated charge carriers can recombine before they reach the respective electrode contact. Therefore, the thick perovskite layer can also contribute in the low R_{sh} .

Meanwhile, the low V_{oc} might be attributed to the non-uniform and uneven layers in the cell. This condition could result in interpenetrating layers, so that the energy level of each layer involved in the cell is disturbed [12]. The high resistance was likely to be caused by the humidity during spin coating process of perovskite and PCBM. A recent report by Huang *et al.* shows that a uniform perovskite layer could be formed when the spin coating was performed under controlled atmosphere, *i.e.* with an argon flow in a glove box [13]. Another factor that could contribute to the high resistance was the presence of holes in the surface of the perovskite layer. The presence of these holes could cause recombination charge at the interface between the perovskite and PCBM [14]. Overall, it was perceived that the poor quality of the perovskite layer has contributed to the low values of the electrical parameters and, thus, low power conversion efficiency was obtained. Optimization of the perovskite layer to obtain a uniform coverage with minimum pinholes will be the focus of our future work based on the findings on the present report.

4. Summary

A perovskite/polymer tandem solar cell was prepared using a solution-based processing, wherein $\text{CH}_3\text{NH}_3\text{PbI}_3$ and PCBM layer was used as an absorber and electron transport layer, respectively. The absorber solution was prepared by mixing $\text{CH}_3\text{NH}_3\text{I}$ with PbI_2 in DMF solvent. The electrical characteristics comprised of an open circuit voltage of 0.31 V, a short circuit current density of 2.53 mA/cm^2 , and a power conversion efficiency of 0.42%. Our results in this work demonstrate that perovskite/polymer tandem solar cell could be produced using a simple and facile fabrication process using wet chemical route. Although further improvement is still required, we believe that the fabrication of low-cost perovskite solar cells with excellent performance can be realized in the future.

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6. References

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