

Synthesizing and characterization of Lead Halide Perovskite Nanocrystals solar cells from reused car batteries

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ABSTRACT:

With the rapid increase of efficiency up to 23.7% during the past few years, hybrid organic-inorganic metal halide perovskite solar cells (PSCs) have become a research “hot spot” for many solar cell researchers. The perovskite materials show various advantages due to unique characteristics of perovskite materials, such as high photo-to-electric conversion efficiency, direct band gap, high light absorption coefficient, high charge-carrier mobility and long electron-hole electron transport distance. The low-cost fabrication techniques together with the high efficiency makes PSCs comparable with Si-based solar cells. This paper begins with the discussion of crystal structures of perovskite based on recent research findings. The following part of this paper discussion of synthetic process of lead iodide perovskite materials from lead-acid battery and Harvesting material from the anodes and cathodes of car battery; synthesizing PbI₂ from the collected materials and compare with pure Lead iodide to know the absolute by XRD peak, depositing lead iodide perovskite nanocrystals. Efficient flexible PSCs are fabricated onto FTO glass substrate by a two-step coating method under ambient condition. By adjusting the concentration of precursor CH₃NH₃I (MAI), the morphology and thickness of perovskite layer is effectively tailored, according to SEM analysis and using TiO₂ as electron transport layer instead of ZnO and CuI instead of spiro-OMeTAD as hole transport layer.

KEYWORDS: perovskite ; thin film ; fabrication ; precursor; photovoltaics.

1. INTRODUCTION

The organic-inorganic halide perovskite solar cells (PSCs) have attracted a great deal of attention of solar cell research community due to an incredible device efficiency improvement from 3.8% to 23.7% since 2009 (Kojima, Teshima, Shirai, & Miyasaka, 2009). The perovskite already gained much attention as a potential replacement of the silicon photovoltaic (PV) devices, which is still occupied the most dominant position in the current PV market, with record efficiency of about 26% (Yoshikawa, Kawasaki, Yoshida, Irie, Konishi, Nakano, Uto, Adachi, Kanematsu, & Uzu, 2017). This small gap of solar cell efficiency attracted recent attention especially from the researchers with experience in dye-sensitized solar cells (DSSCs) or organic solar cells because some materials can be used in both PSCs and organic solar cells. The structure of PSCs also origins from the device structure

of DSSCs. The perovskite materials have been demonstrated with largely tunable band gap (e.g., $\text{CH}_3\text{NH}_3\text{PbX}_3$ has a band gap from 1.5 eV to 2.3 eV) (Yoshikawa, Kawasaki, Yoshida, Irie, Konishi, Nakano, Uto, Adachi, Kanematsu, & Uzu, 2017). and great light absorption coefficient (higher than 10^4 cm^{-2}) (Park, 2015), which is similar to other thin film solar cell materials such as CdTe (Rangel-Cárdenas & Sobral, 2017) and copper zinc tin sulfide (CZTS) (Shi & Jayatissa, 2017). Its low-cost and convenient fabrication techniques also serve as the possible advantages over silicon-based devices that require complicated and costly high-vacuum deposition methods. Reports of successful cell fabrication on flexible substrates even indicated a greater possibility to the large-scale roll-to-roll manufacturing of PSCs that can be used in the industries (Kumar, Yantara, Dharani, Graetzel, Mhaisalkar, Boix, & Mathews, 2013).

The initial meaning of “perovskite” was about the crystal structure of calcium titanate (CaTiO_3), which was discovered in 1839 by the German mineralogist Gustav Rose and was named by the Russian mineralogist Lev Perovski. Since then, the term “perovskite” was referred to all compounds with the same crystal structure as calcium titanate. The perovskite light absorption layer has a general formula of ABX_3 , where A is an organic cation (e.g., methyl-ammonium CH_3NH_3^+), B is a metal cation (e.g., Pb^{2+}) and X stands for the halide anion (e.g., I^-). The first record of perovskite-based solar cell efficiency, however, was reported by Miyasaka et al. (Kojima, Teshima, Shirai, & Miyasaka, 2009) only less than one decade ago. They reported an efficiency of 3.8% based on a DSSC structure. Due to the application of liquid electrolyte in the hole-transporting material (HTM), the stability of solar cell was very weak and did not attract much attention. Similar trial was done by Park et al. (Im, Lee, C., Lee, Park, S., Park, 2011) with the increased efficiency of 6.5% but stability was still the main problem because of the instability of HTM layer due to the liquid medium. (Shin, Yang, Noh, Suk, Jeon, Park, Kim, Seong, & Seok 2015).

1.1. Structures of Perovskite Solar Cells:

The perovskite materials have a general crystal structure described as ABX_3 , where “A” and “B” are cations with varied sizes and “X” is an anion. A typical unit cell structure of a basic perovskite compound is shown in Figure 1. Organometallic halide perovskites include an organic cation (e.g., methyl-ammonium CH_3NH_3^+ , ethyl-ammonium $\text{CH}_3\text{CH}_2\text{NH}_3^+$, formamidinium $\text{NH}_2\text{CH}=\text{NH}_2^+$), a metal cation of carbon family (i.e., Ge^{2+} , Sn^{2+} , Pb^{2+}) and a halogen anion (i.e., F^- , Cl^- , Br^- , I^-). Among them, methyl-ammonium-lead-iodide (MAPbI_3) is the most widely used perovskite light absorber. Some recent research efforts also replaced lead with other metal ions due to the concern of toxicity of lead during device fabrication, especially for the future large-scale manufacturing (Jain, Castelli, Hautier, Bailey, & Jacobson, 2013). In addition, several organic cations (CH_3NH_3^+ and $\text{NH}_2\text{CH}=\text{NH}_2^+$), inorganic cations (Cs_2^+ and Sn_2^+) and halide anions (Br^- , Cl^- and I^-) have been used to improve the efficiency and stability.

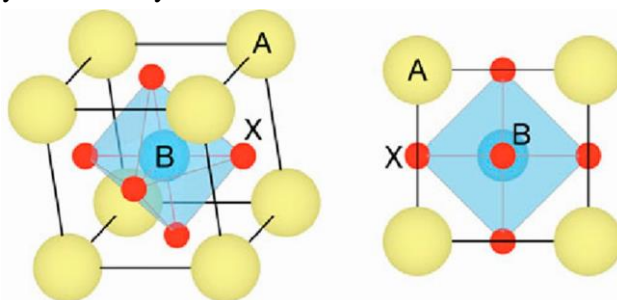


Figure 1. A generic perovskite crystal structure of the form ABX_3 (Bischak, Hetherington, Aloni, Ogletree, Limmer, & Ginsberg, 2017).

Perovskite materials have different phases depending on the change of temperature. When temperature is lower than 100 K, the perovskite displayed a stable orthorhombic (γ) phase. With temperature increased to 160 K, the tetragonal (β) phase started to appear and replace the original orthorhombic (γ) phase (Kawamura, Mashiyama, & Hasebe, 2002). As temperature increases further to about 330 K, the tetragonal (β) phase started being replaced by another stable cubic (α) phase (Whitfield, Herron, Guise, Page, Cheng, Milas, & Crawford, 2016). Figure (2) displayed all those three crystal structures. The tetragonal-cubic phase transition at higher temperature partially influences the thermal stability of perovskite materials. Formamidinium iodide ($\text{HC}(\text{NH}_2)_2\text{PbI}_3$), for example, has a phase transition occurred at a higher temperature, indicating that it is relatively stable compared with common MAPbI_3 . Moreover, a recent report suggested that light soaking could also trigger the reversible phase transition of perovskite materials (Bischak, Hetherington, Aloni, Ogletree, Limmer, & Ginsberg, 2017) but more efforts are required to demonstrate this behavior.

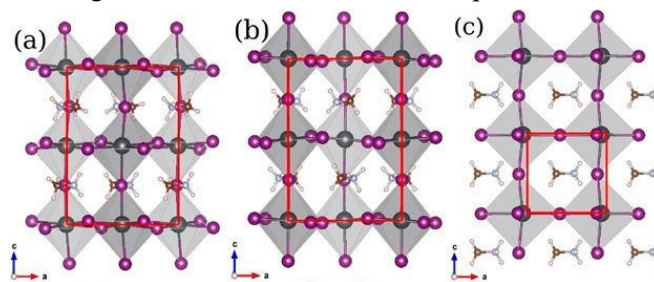


Figure 2. Comparison of (a) orthorhombic; (b) tetragonal and (c) cubic perovskite phases obtained from structural optimization (Korshunova, Winterfeld, Beenken, & Runge, 2016).

1.2. Working Principle of Perovskite Solar Cells:

According to PIN junction Principle, When the photons lies on perovskite solar cell electrons (negative charge) move from valence band (V.B) to Conduction band in perovskite layer (active layer) and that's distance in called the band gap. they leave their place empty and that's called a hole (positive charge). Then electrons jump to the next layer which is less in Conduction (i.e. electrons jump from the high conduction to the low conduction) Zinc Oxide layer (Electron Injection Layer), then jump to FTO glass sub- strate (anode) of our solar cell. In the same way holes jump to Copper Iodide (Hole Injection Layer) as shown in figure (3) then to Silver (Ag) cathode of our solar cell. Now we can use electrons to make a circuit and generate a current (I) constantly.

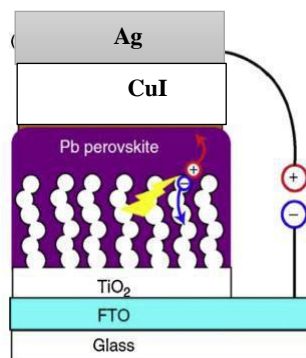


Figure 3. Working principle of perovskite solar cell (FTO/TiO₂/perovskite/CuI/Ag) structure.

1.3.Light Source:

The solar spectrum of sunlight travelling through the atmosphere of earth is attenuated by scattering and absorption. To characterize the performance of solar cells under standardized sunlight conditions, the air mass (AM) coefficient is commonly used and calculated with this formula when the curvature of the earth is considered

$$AM = \frac{1}{\cos\theta + 0.50572(96.7995 - \theta)^{-1.6364}} \quad (1)$$

θ is the zenith angle, which means the angle between sunlight and the normal of horizon. [18] As this definition suggests, AM 0 is suitable for sunlight at the outer space and AM 1 is that at sea level with the sun directly overhead in equatorial and tropical regions. AM 1.5, however, can be reached at most space on earth with a value of $\theta = 48.2^\circ$ and the power of which approaching 1000 W.m^{-2} . Taking diffusion radiation into consideration, AM 1.5G (global) is widely used for the standard measurement of solar cells. In laboratories, solar simulator is a traditional apparatus to simulate AM 1.5G sunlight and get the performance of solar cells. As such, its quality will directly affect the accuracy of measurement.

2. EXPERIMENTAL PART

2.1. Chemical:

- Lead (anode) and lead Dioxide (cathode) of car battery (12 V ,799.7g lead).
- HCl (Hydrochloric Acid), Acetic Acid (CH_3COOH),
- Nitric Acid (HNO_3) and Hydroiodic Acid (HI) lab teach.
- Dimethylformamide (DMF) of Sigma-Aldrich (#227056, > 99.8%)
- Titanium dioxide supplied by Alpha chemika™ Mumbai 200002, India.
- Cupper Iodide (CuI) of Sigma-Aldrich (#205540, > 98%)
- Fluorine tin oxide (FTO $\sim 7 \Omega/\text{sq}$)
- Methylamine (CH_3NH_2) in methanol from Sigma-Aldrich (#395048).

2.2. Apparatus:

- Magnetic bar and magnetic stirrer type lab teach.
- Muffle furnace ($T > 600^\circ\text{C}$), hot plate ($T > 500^\circ\text{C}$) Spin coating (> 4000 r. p. m. for 60s).
- Scanning electron microscopy (SEM, JSM-7600 F, Jeol).
- X-ray diffraction (XRD, Rigaku ATX-XRD with Cu K α radiation ($k = 1.5405 \text{ \AA}$) in 2θ ranging from 10° to 20°).

2.3. Harvesting material from the anodes and cathodes of car battery:

First disconnect the car battery with metal cutter. The acid electrolyte was poured out and carefully collected, and the electrodes as well as the inner wall of car battery were rinsed several times by clean water. The electrolyte contains concentrated sulfuric acid (H_2SO_4). The obtained car battery was dried in the ambient condition for 3 days. The dry car battery was disassembled from the top lid and then sawed from the sides to extract the electrode panels. After disassembling, the lead-derived materials were scratched off i.e. Lead (anode) and Lead Dioxide (cathode) from the current collectors separately, and washed with dilute HCl (Hydrochloric Acid) and clean water sequentially. The collected materials were ground into powders for further synthesis. Lead Dioxide (PbO_2) is to be converted into lead oxide (PbO) by roasting it at $600^\circ C$ for 5 hours by placing lead Dioxide (PbO_2) in a Muffle furnace by using Ceramic Crucible. After heating Lead Dioxide at $600^\circ C$ for 5 hours it has to be cooled at room temperature. The color of the powder was changes from dark brown to yellow color. L Preparation of Lead Iodide from Lead Acetate, dissolve 3gms of PbO (Lead Oxide) in 5 ml of Acetic Acid. Preparation of Lead Iodide from Lead Nitrate, dissolve 3 gm of Pb (Lead) in 5 ml of Nitric Acid by constant stirring in a magnetic stirrer then Dissolve 10 ml of potassium iodide, Potassium iodide is act as a catalyst for to increase the rate of reaction. Stirring the solutions for 30 minutes at 500 rpm by using magnetic stirrer. Leaving the solution in aerobic condition for 1 day then purify the solution by using centrifuge machine, The solution has to be filled in a centrifuge tubes then add Deionized water to the solution then centrifuge the solution at 5000 rpm for 5 minutes, repeat the procedure for 3 times for to remove the acidic concentration completely, due to density variation the precipitate will settle down then the acidic concentration has to be removed. After centrifuging the solution, the solution has to be dried in aerobic condition during the entire procedure the solution has to be placed in a fume hood or fume cupboard.

2.4. Preparation of methylammonium iodide (CH_3NH_3I) :

Firstly, HI was mixed with Methylamine (CH_3NH_2) in methanol and stirred in ice bath until white crystals were formed. Secondly, methanol was removed then the solution was filtrated to produce white crystals of CH_3NH_3I .

2.5. Device fabrication:

Organolead halide perovskite solar cell consist of five layers as following:

2.5.1. First layer of perovskite solar cell:

Before using of FTO glass substrate, FTO glass has to be cleaned with IPA (Isopropyl Alcohol) by dipping FTO glass in IPA (Isopropyl Alcohol) for 30 minutes. And used ohmmeter to know the conductive side.

2.5.2. Electron Transport Layer(ETL):

Using TiO_2 as electron transport layer instead of ZnO .

TiO_2 coated on the conductor face of FTO by using the spin-coating method at 3000 r.p.m.

2.5.3. Perovskite Light-Absorbing Layer:

Dissolve 924gm of (PbI₂) in 2 ml of N, N- dimethylformamide DMF, (at the speed of 1000 r.p.m. for 10 s then 2500 r.p.m for 30 s), and then dried on an 80 °C hot plate for 1 min. Later, the solution of CH₃NH₃I in Isopropyl Alcohol then dropped onto the film of PbI₂ and spin coated (at the speed of 1000 r.p.m. for 10 s then 2500 r.p.m for 30 s) after waiting for 2 min. After that, a transparent brown perovskite film was obtained, followed with annealing on hotplate with temperature of 100 °C for 15 min, the brown film changed into a black perovskite film but still transparent.

2.5.4. Hole Transport Layer(HTL):

CuI (HTL) was then deposited by spin-coating at 4000 r.p.m. for 30 seconds.

2.5.5. Last layer:

80 nm of silver was thermally evaporated on top of the device. Thermal evaporator at a base pressure of 10⁻⁵ mbar.

3. RESULT AND DISCUSSION

3.1. Compare PbO of car battery with PbO of Sigma Aldrich:

Lead Dioxide (PbO₂) is to be convert into lead oxide (PbO) by roasting it at 600°C for 5 hours by placing lead Dioxide (PbO₂) in a Muffle furnace by using Ceramic Crucible. After heating Lead Dioxide at 600°C for 5 hours it has to be cooled at room temperature. The color of the powder was changes from dark brown to yellow color. By comparing XRD analysis on the high-purity PbO powder (Sigma-Aldrich, #15338, >99.0%) and the PbO particles after the annealing of PbO₂ particles for 5 hours. As shown in the figure 4, PbO particles after annealing is pure.

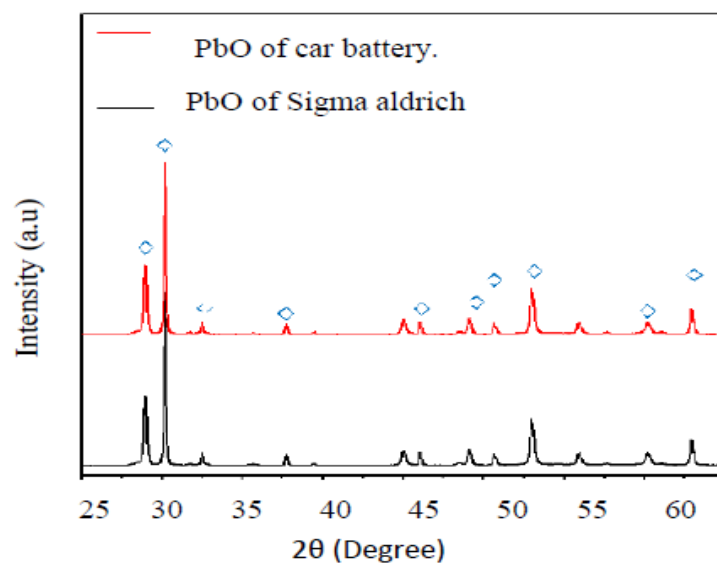


Figure 4. XRD analysis on the high-purity PbO powder (Sigma-Aldrich, #15338, >99.0%) and the PbO particles after the annealing of PbO₂ particles for 5 hours.

3.2. Compare PbI₂ of car battery with PbI₂ of Sigma Aldrich:

XRD analysis on the high-purity PbI₂ powder (Sigma-Aldrich, #211168, >99.0%) and the PbI₂ powders synthesized from the cathodes and anodes of car batteries. As shown in the figure 5.

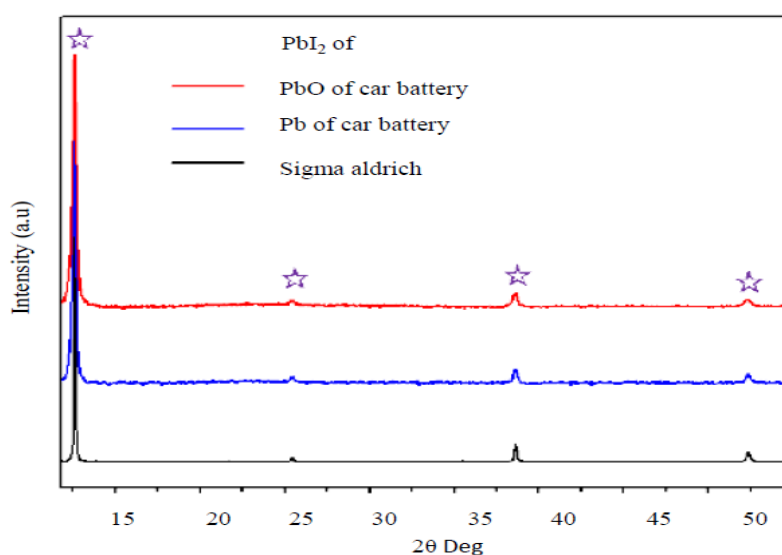


Figure 5. XRD study on pure PbI₂ powder (Sigma-Aldrich, #211168, >99.0%) and the PbI₂ precipitates produced from the cathodes and anodes of car batteries.

3.3.XRD peak of perovskite solar cell :

XRD measurements on our perovskite thin films showed typical perovskite (110) and (220) peaks at 14.2° and 28.5° , respectively (Fig.6a).

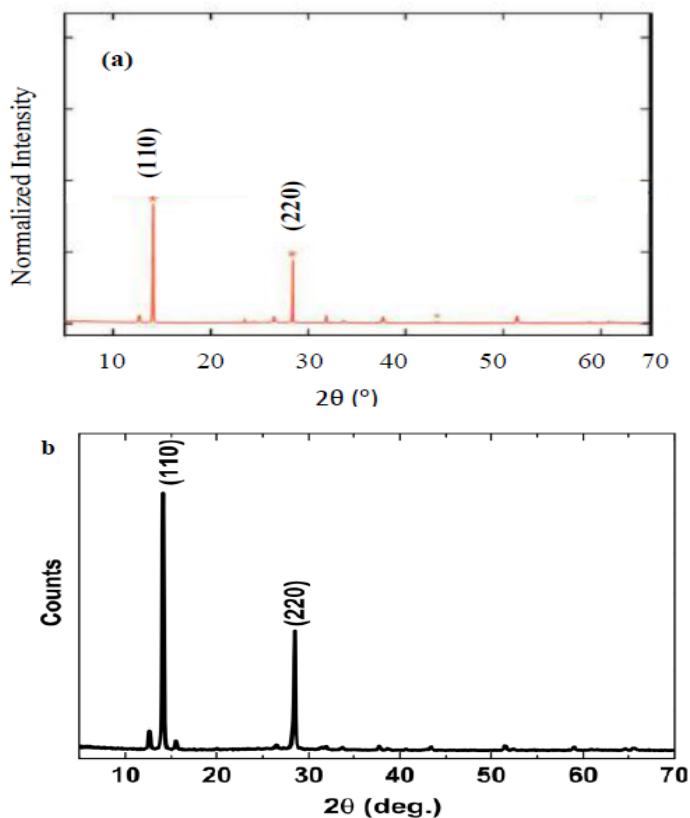


Figure6.(a) X-ray diffraction of the spin coated perovskite film showing (110) and (220) peaks. (Liu, Johnston,& Snaith, 2013) (b) Standard peak of perovskite thin film to comparable with our film.

3.4. Thickness of perovskite device:

a schematic illustration of the energy levels of hole transporting material (HTM) and electron transporting material (ETM) well aligned with the perovskite leading to high charge separation. Based on cross-section SEM images of PSCs in Fig. 7(a),(b) respectively, it is noticed that the concentration of MAI solution could effectively control the thickness of the perovskite as well, for instance, with the concentration of MAI solute decreasing from 12 mg ml^{-1} and 9 mg ml^{-1} , the thickness of perovskite film reduces dramatically from 500 nm to 400 nm Therefore, it is possible that flexible PSCs with good transparency could be fabricated by effectively changing the concentration of MAI precursor.

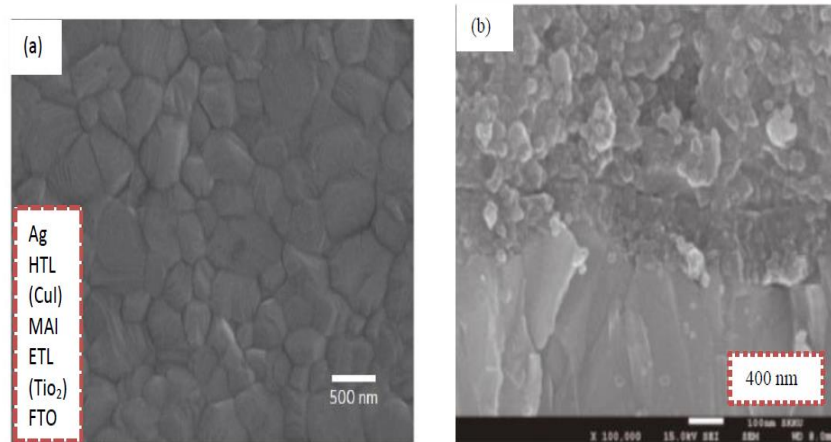


Figure 7. a,b, SEM image of perovskite device with normal and high resolution.

3.5. Temperature effect on efficiency:

We test our cell under various temperatures to determine the optimal temperature which provides the maximum efficiency, the cell achieves the maximum efficiency figure (9) which occurs at 35 °C .

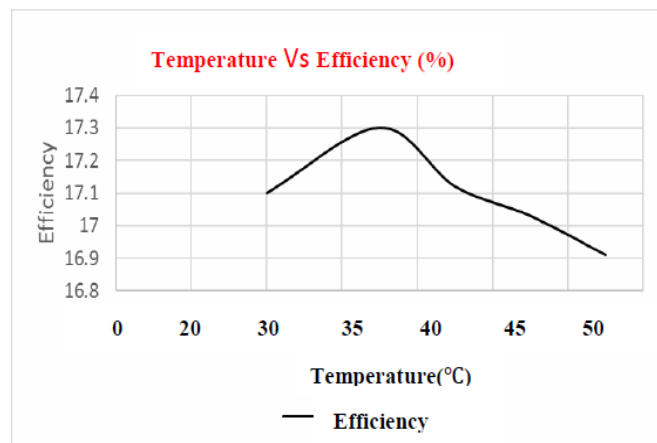


Figure (8). Efficiency change with different temperature.

3.6. Effect of time during day on power :

We test our cell under several times to control the best time which provides the maximum output power , the cell achieves the maximum output power figure (10) which occurs at 12 p m .

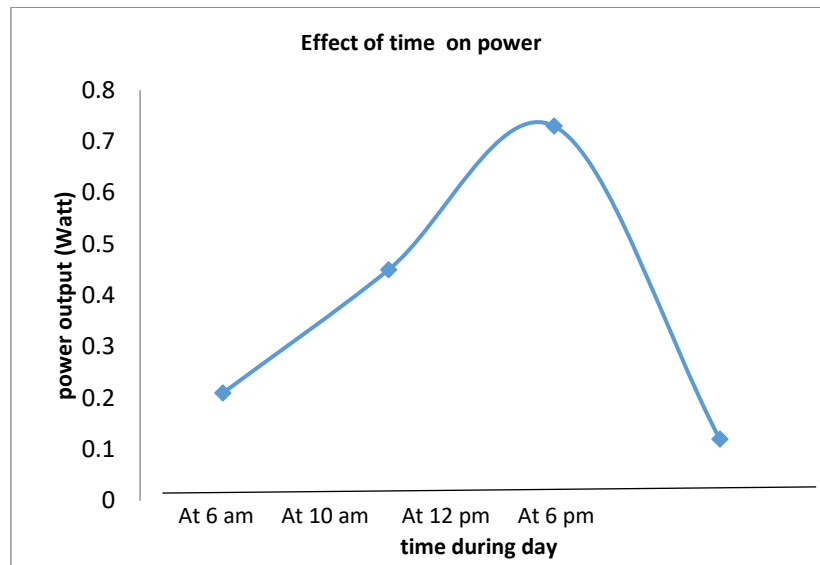


Figure (9). Power change with different day time.

3.7. I-V Characteristics :

In this section we measure FF and efficiency of perovskite solar cell. The current–voltage curves of solar cells were measured by using a Keithley 2400 source measure unit under AM1.5G illumination with light intensity of 100mWcm^{-2} .

3.7.1.Fill factor:

The fill factor is the ratio of the actual maximum obtainable power to the product of the open circuit voltage and short circuit current. This is a key parameter in evaluating performance. Fill Factor is a measure of the “squareness” of the IV curve. The fill factor is essentially a measure of quality of solar cell. To calculate the fill factor of perovskite solar cell we use this formula:

$$\mathbf{FF} = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (2)$$

Where

FF: fill factor

V_m : maximum value of voltage (V)

I_m : maximum value of current (mA)

V_{oc} : open circuit voltage in (V)

I_{sc} : short circuit current (mA)

The value of each parameter shown in the **table (1)**.

table (1). cell performance of perovskite solar cell

V_{oc} (V)	I_{sc} (mA)	V_m (V)	I_m (mA)
1.1	23.969	0.9	23.21

$$\mathbf{FF} = \frac{V_m I_m}{V_{oc} I_{sc}} = \frac{0.9 \times 23.21}{1.1 \times 23.969} = 0.76$$

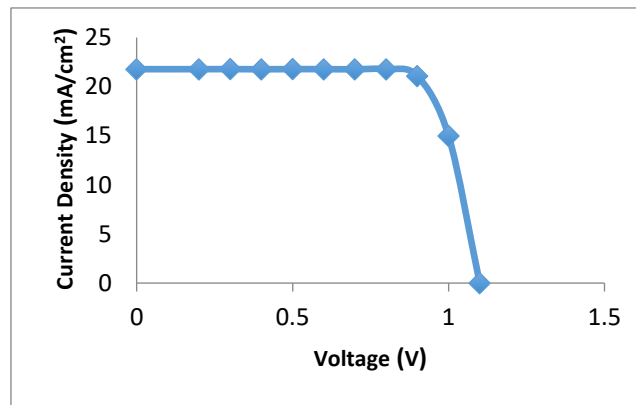
3.7.2. Efficiency of perovskite solar cell:

The key parameters representing the devices performance can be given through this test, involving the short circuit current (I_{sc}) or current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (η) and their relationship embodies in this formula:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{I_{sc} V_{oc} FF}{P_{in} A_{aperture}} = \frac{J_{sc} V_{oc} FF}{P_{in}} \quad (3)$$

$$\eta = \frac{I_{sc} V_{oc} FF}{P_{in} A_{aperture}} = \frac{23.969 \times 10^{-3} \times 1.1 \times 0.76}{1000 \times 1.1 \times 10^{-4}} \times 100\% = 18.2\%$$

where P_{in} is the irradiance of the incident light received by the test cell, P_{out} is the maximum output power of this cell as shown in figure (11), and $A_{aperture}$ is the aperture area for the incident light.



Figure(10).J-V curve of PSCs

4. CONCLUSION

Perovskite solar cells represent a huge opportunity for large-scale, affordable 3rd-generation solar energy. In this paper, we review the advances in the recent developments, as well as the fundamentals and basic structures of the perovskite solar cells. The versatility in the fabrication techniques of the perovskite light-absorbing layer, which include the solution-deposition method, vapour-deposition method, the vapour-assisted solution method and spin coating. Herein our method choice spin coating easy and faster than another methods. Reusing car battery instead of disposal car battery to synthesis lead iodide (PbI_2) and using Copper iodide (CuI) in place of spiro-OMeTAD as p-type (HTL) layer more effective and stable than another kind of materials, Impedance spectroscopy revealed that CuI exhibited two orders of magnitude higher electrical conductivity than spiro-OMeTAD that allowed appreciably higher fill factor(FF). Numerous research efforts on both PSC efficiency improvements and deeper understanding about perovskite materials' outstanding electrical and optical properties, such as largely-tunable band gaps for light absorption, high absorption coefficients, large carrier diffusion lengths, great carrier mobility, have been established during the past few years. The current PSCs already combined structural advantages of both DSSCs and thin film PV since the discovery of perovskite and become a new challenger for Si-based PV dominant market share, not only due to record 23.7% efficiency for small area but also comparable larger-area device efficiency. The vast discovery and successful application of organic/inorganic charge transport materials and blocking layers also assisted the formation and crystallization of perovskites and helped charge transfers at the interfaces. The PSCs still have great barriers for further improvements. The biggest problem comes

with the natural instability of perovskite materials, especially the most widely-used MAPbI₃. The phase transition within the range of solar cell operation temperature brought problems on device usage. The instability with varying temperature and pressure leads extra concerns for device fabrication. The moisture, UV light and oxygen would also bring irreversible damage to the perovskite layers, which largely reduced the device stability and commercialization of PSC. The efforts such as elemental adjusting, device sealing and extra blocking layer inside the device had been tried to solve these problems but more stability tests under harsh environments are strongly suggested for PSCs to reach the required standard. Other drawbacks such as J-V hysteresis and toxicity of lead made it difficult to further improve the performance of PSCs. While the mechanism of hysteresis was still inconclusive, the lead toxic has attracted many research efforts on considering the non-toxic replacement of perovskite materials. Research work found out that all candidates, from the neighborhood Sn, Bi and new candidates as Cs, Ge, suffered a great loss of J_{sc}, which directly leads to the huge loss in PCE. A more complicated replacement profile might be the solution of lead-free PSCs. Although efforts claimed low hysteresis in some PSCs, deep theoretical understanding and standardized testing protocol is suggested for PSCs. Perovskite, compared with other PV techniques (thin film, organic, dye-sensitized), could be the best alternative solar absorber. As efforts on better perovskite layer formation and longer device durability, even the lead-based PSCs could be able to share a certain part of PV market.

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