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Review article

Electrodeposition of organic–inorganic tri-halide perovskites solar cell

U.A. Charles[a,b,*], M.A. Ibrahim[a,**], M.A.M. Teridi[a]

[a] Solar Energy Research Institute, The National University of Malaysia (UKM), 43600 Bangi, Selangor, Malaysia
[b] Cahams Research Consultant Sdn Bhd, 74 B Taman Sri Langat Kajang 43000 Kajang, Malaysia

HIGHLIGHTS

- Electrodeposition is a versatile route for large-scale production of solar cell.
- Electrodeposition of perovskite solar cell is scalable and has been demonstrated.
- Optimization of deposits is a prerequisite for high performance solar cells.
- Determinants of surface quality of electrodeposited materials are reviewed.

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ABSTRACT

Perovskite ($CH_3NH_3PbI_3$) semiconductor materials are promising high-performance light energy absorber for solar cell application. However, the power conversion efficiency of perovskite solar cell is severely affected by the surface quality of the deposited thin film. Spin coating is a low-cost and widely used deposition technique for perovskite solar cell. Notably, film deposited by spin coating evolves surface hydroxide and defeats from uncontrolled precipitation and inter-diffusion reaction. Alternatively, vapor deposition (VD) method produces uniform thin film but requires precise control of complex thermodynamic parameters which makes the technique unsuitable for large scale production. Most deposition techniques for perovskite require tedious surface optimization to improve the surface quality of deposits. Optimization of perovskite surface is necessary to significantly improve device structure and electrical output. In this review, electrodeposition of perovskite solar cell is demonstrated as a scalable and reproducible technique to fabricate uniform and smooth thin film surface that circumvents the need for high vacuum environment. Electrodeposition is achieved at low temperatures, supports precise control and optimization of deposits for efficient charge transfer.

1. Introduction

Deposition techniques to grow thin film solar cell has improved over the years and enhances the surface quality of deposits. The improvement has spurred the performance of solar cells and supports efficient charge transfer and minimizes wastages of useful materials [1]. The performance of organometallic perovskites solar cell based on $MAPbX_3$ ($MA = CH_3NH^{3+}$; X = Cl, Br or I) has shown to be an efficient light absorbing material for future thin film solar cell. The promising qualities of perovskite have propelled the use of the material at the forefront of solar cell innovations. Their solution processability, high crystallinity with direct and tunable bandgaps as well as high hole/electron transport capability makes perovskite a choice absorber layer material for solar cell [2,3]. Over the period of seven years of research, the efficiency of perovskite solar cell based on mesoscopic and planar-structure reached power conversion efficiency (PCE) of 15% [4–12] and has spurred from 16.13% to 20.75% with the incorporation of different light management schemes (such as; flat glass, slotted prism, inverted prism, slotted prism and inverted prism with ITO) [13] and recently increased to 20.80% [14]. The sharp increase in PCE over short period of research is an indication that further improvement will lead to significant breakthrough in thin film solar cell. This review highlights transformative shift and improvement in processing solar cell material poised to substantially enhance the performance by optimizing their surface quality (see Table 1).

Zhou et al. [15] adopted interface engineering and achieve PCE of 19.3% although the approach is not cost-effective to develop future solar cell. The development of a low-cost and efficient perovskite solar cell that supports large scale production requires a cost-effective and reproducible deposition technique. Interest in improving the surface

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[*] Corresponding author. Solar Energy Research Institute, The National University of Malaysia (UKM), 43600 Bangi, Selangor, Malaysia.
[**] Corresponding author.
E-mail address: charles@ukm.edu.my (U.A. Charles).

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Table 1
Stoichiometry of three-compositional variables of perovskite material.

Stoichiometry of perovskite structure	Elements
A	Ce^{3+}, Dy^{3+}, Er^{3+}, Eu^{3+}, Gd^{3+}, Ho^{3+}, LA^{3+}, Lu^{3+}, Nd^{3+}, Sm^{3+}, Tb^{3+}, Yb^{3+}
B	Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, In^{3+}, and Sc^{3+}
X	Halogen or Oxygen

quality of solar cell is driven by the need to enhance the transfer of charges relative to device performance. The performance of perovskite solar cell has been affected by high surface roughness associated with widely used 'spin coating technique' indicating a pressing need for an alternative deposition technique for perovskite layer [16–27].

Over the years, a well-known deposition technique used for processing perovskite materials comprising PbX_2 and MAX in solvent such as γ-butyrolactone [9] or dimethylformamide [10] on mesoporous or planar substrate has been mainly by spin coating. Spin coating has been widely used in preference to other deposition technique as a convenient and cheap deposition technique [6,12,13]. In contrary, spin coating deposition process evolves rapid reaction and uncontrolled precipitation resulting to high surface roughness and large morphological differences. This is because reaction occurring at the interface affects the smoothness of the deposited film and impedes device performance by inferring with the movement of charge carriers [12,13]. Therefore the tendency for the grain structures of the deposited film to change during the intercalation reaction leading to scattered voids of adjacent grains increases with spin coating technique.

To sidetrack high surface roughness associated with spin-coated film, vapor deposition technique has been considered appropriate to create uniform thin film of perovskite [11,25]. Nevertheless, vapor deposition is very complex technique and requires high vacuum and precise control of thermodynamic parameters relative to temperature and pressure making the technique unsuitable for large scale production at low-cost [21]. Among other deposition techniques to achieve smooth and flat surface in perovskite solar cell include two-step sequential solution process [10], vapor assisted solution method [28] and solution-processed precursor stacking method [29,30].

An efficient two-step deposition technique for perovskite solar cell (Fig. 1) has been demonstrated using PbO as starting material which is not possible with spin-coating method. Spin-coating PbO as starting material onto a mesoporous or planar substrate initiates inter-diffusion reaction with MAX. Thus, conventional spin-coating method imposes significant challenges to large scale fabrication of uniformly smooth and flat thin film of perovskite required for efficient charge transfer [31]. Electrodeposition technique is environmentally friendlier, reproducible and those not require high temperature treatment or vacuum environment to fabricate solar cell [30]. Precise control of the deposition parameters is among the approach used to minimize wastages of useful materials. Electrodeposition of perovskite represents an efficient technique to vary film thickness and surface profile of deposited thin film. The deposition technique allows for the formation of different layers of solar cell as illustrated in Fig. 1 using a case PbO is used as a starting material to grow perovskite film.

Electrodeposition method is a bottom-up approach that is used for uniform deposition of thin layer. Fig. 1 shows how gradual electrochemical reaction starting with PbO diffusing to the surface of an electrode (substrate coated with TiO_2) to form a thin layer of perovskite. The uniqueness of electrodeposition method confines to its ability to precisely control the thermodynamic deposition parameters that are relative to specific film thickness and the enhancement of smooth surface profile [30]. Electrochemical deposition technique has been successfully used to deposit PbO on the mesoscopic TiO_2 layer. The deposition of iodinated PbI_2 initiated inter-diffusion reaction that facilitated the formation of $CH_3NH_3PbI_3$ which is an efficient light energy absorber for solar cell [32]. Alternatively, electrodeposition of perovskite by direct conversion of PbO on *c*-TiO_2 coated FTO glass substrate with CH_3NH_3I layer represents an efficient technique to produces flat and uniform thin film [31] for various optoelectronic devices. Uniformly electrodeposited thin film of perovskite improves power conversion efficiency of devices by careful control of the deposits, concentration of the electrolytic solution and deposition time [33]. Precise optimization of the deposited thin film enables for efficient harvest of more incident photons from wider spectral wavelength to generate more photo-induced charge carriers to improve device performance.

2. Stoichiometry of perovskite structure

The stoichiometry of perovskite structure follows three-compositional variables denoted by ABX_3. "A" and "B" are cations and X is anion. Elements constituting A, B and X [34,35]:

Perovskite $CH_3NH_3PbX_3$ sensitizer expressed as 'ABX_3' comprising A and B as cations 12 and contains 6 coordinate with X anions to form cuboctahedral and octahedral geometries [36]. The attractive optoelectronic properties exhibited by perovskite materials are relative to their crystal structure dimensionality and correlates to their superconductivity [37,38]. This implies that a change in the crystal structure could lead to a new functionality since their properties are subject to crystal orientation. The stability of perovskite structure solely depend on the distance ratio (A − X) to (B − X) also known as tolerance factor (eq. (1)) [39].

$$t = \frac{(R_{A+}R_X}{\sqrt{2\,(\mathrm{R}_B + R_X)}} \qquad (1)$$

The stabilized cubic phase represented as $(\mathrm{R_A} + \mathrm{R_X}) = 2^{1/2}(\mathrm{R_B} + \mathrm{R_X})$ and distorted octahedral [BX6] is changed from perovskite-type crystals of Lead-halide to a unique optical crystal structure. Organo

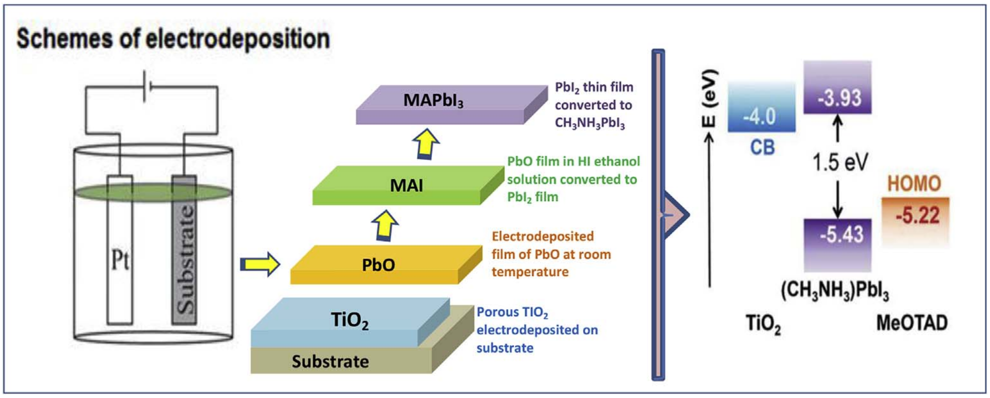

Fig. 1. Schematic of perovskite $CH_3NH_3PbI_3$ formation onto compact TiO_2 on FTO substrate by electrodepositing PbO to initiate in-situ reaction to form perovskite layer.