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Rapid fabrication of efficient P-type perovskite-sensitized solar cells using hot-air drying method

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Abstract

The successful development of organic-inorganic perovskite materials mainly based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ has improved the PCE of solar cells significantly and reduced the fabrication cost relatively. The majority of the researches focused on studying different ways of improving the performance and stability of perovskite devices with less attention paid to minimizing the time of fabrication. The reduction of fabrication time can simultaneously reduce the fabrication cost and boost the industrial manufacturing capability. In this work, we report a simple and rapid method of making $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer at ambient laboratory conditions and applying it for advancing the photon-to-electricity conversion efficiency of liquid-state CuO-based perovskite-sensitized solar cells. The whole fabrication process starting from electrodeposition of CuO to sandwiching counter electrode entails less than 10 min and the device efficiency reaches up to 0.35% under one sun illumination.

1. Introduction

Organic-inorganic metal halide perovskite mainly based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ is an efficient light absorber capable of improving the PCE of solar cells and reduced the fabrication cost. Perovskite materials possess high carrier mobilities, large defect tolerance, tunable band gap, long diffusion length and low exciton binding energy [1,2]. However, the standard fabrication procedure, where the $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase is usually formed by dissolving perovskite salts ($\text{CH}_3\text{NH}_3\text{I}$ and PbI_2) in a polar solvent before being spin coated and annealed on a substrate [3,4], is slightly time-consuming and the process must be conducted in an inert atmosphere. Therefore, methods that utilize shorter fabrication time and capable for ambient air processing must be developed for commercialization purpose. $\text{CH}_3\text{NH}_3\text{PbI}_3$ can also be used to replace organic dye as sensitizer in liquid-state p-type dye-sensitized solar cells (DSSCs) [5]. The development of p-type DSSCs, where the light absorbing material is sensitized on a photocathode, is very important for realising the production of highly efficient tandem solar cells. To date, one of the potential photocathodes for DSSCs is CuO because CuO is naturally abundant, cost-effective, non-toxic and highly conductive. Suzuki et al. were the first group that utilised CuO as photocathode sensitised with different dyes and obtained 0.3 mA cm⁻², 0.115 V, 0.011% for J_{sc} , V_{oc} and PCE, respectively [6]. Despite this success, the study on CuO-based DSSCs currently is very scarce and the recorded efficiency of the CuO-based devices hardly surpasses 0.2% [7]. Here, we report on the first development of liquid-state CuO-based perovskite-sensitized solar cells (PSCs). We also present a cheap, rapid hot-air drying method for making $\text{CH}_3\text{NH}_3\text{PbI}_3$ films which enables complete fabrication of liquid-state PSCs in

less than 10 min. This work is an extension from our previous report related to rapid fabrication of CuO by electrodeposition [8].

2. Experimental

FTO substrates (Pilkington, TEC 8) are cleaned successively using soapy water, 2-propanol, deionised water, acetone and ethanol, in ultrasonic bath for 10 min. The substrates were kept in ethanol prior to fabrication process. CuO was deposited on FTO substrates using a method reported by Sagu et al. [8]. Basically, CuO was electrodeposited from aqueous solution containing 25 mM CuSO₄ at 1.5 V with respect to Ag/AgCl/3M KCl for 120 s, followed by washing with deionised water before annealing at 500°C for 60 s. After cooling at room temperature, the FTO/CuO electrodes were coated with CH₃NH₃PbI₃ using rapid heat gun drying method. 20 mL of 1 M PbI₂ in dimethylformamide (DMF) was casted onto CuO/FTO and allowed to fill the pores for 1 min. Then the excess PbI₂ was removed by tissue before using a hot-air dryer set at 70°C. Subsequently, the electrode was dipped in CH₃NH₃I solution (10 mg/mL isopropanol) for 1 min followed by drying at 70°C for 1 min using the heat-gun dryer. The FTO/CuO/CH₃NH₃PbI₃ electrodes were filled with the I/I₃ electrolyte (500 mM LiI, 250 mM I₂, 30 mM CO(NH₂)₂ and 300 mM tert-butylpyridine in anhydrous ethyl acetate) and sandwiched with Pt as a counter electrode. The whole fabrication process was performed in ambient laboratory atmosphere without humidity controlling system.

3. Results and discussion

The X-ray diffraction (XRD) pattern of CuO films deposited on FTO substrates with and without CH₃NH₃PbI₃ sensitizer are shown in Fig. 1(a). Characteristic peaks at 35.7°, 38.8°, 54° corresponding to (1 1 1), (1 1 1) and (0 2 0) crystal planes, respectively, were detected. These peaks can be indexed to the monoclinic structure of CuO (JCPDS card No. 48-1548) [9]. With the help of Scherrer formula and the broadening of (1 1 1) diffraction peak, the crystallite size was estimated to be 32 nm. Peaks belonging to perovskite were observed when the CuO sample was coated with CH₃NH₃PbI₃. However, strong diffraction peak particularly at 12.7°, which was assigned to the (0 0 1) peak of a photo-inactive cubic PbI₂, is noticeable due to incomplete conversion of PbI₂ to perovskite [10]. This could be attributed to the employment of ambient air processing approach, the low temperature of hot air treatment (70°C) and short soaking time in CH₃-NH₃I solution. The existence of PbI₂ layer might be useful for surface passivation because the layer can inhibit recombination process between electrons and holes at the perovskite/photocathode interface [11].

The FTO/CuO/perovskite film showed significant light absorption in the range of visible to near infrared as represented in Fig. 1(b). The absorption spectra indicated sharp absorption edge at 760 nm which is consistent with the bandgap of perovskite (~1.6 eV) [12]. From this analysis, it can be expected that the p-type solar cells will deliver high efficiency due to improved current generation. One of the prerequisites for achieving high PCE in PSCs is to obtain high surface coverage of perovskite film. As observed from Fig. 1(c), the hot-air treatment employed for fabricating CH₃-NH₃PbI₃ layer homogeneously covered the surface of FTO-coated CuO and only few pinholes were observed. Thus, there should be improvement in the performance of the fabricated devices when using this method.

To analyze the effect of the perovskite sensitization method, iodide/triiodide electrolyte was added to the cell system and sandwiched with platinum sheet for creating a liquid-state CuO-based PSC with configuration FTO/CuO/CH₃NH₃PbI₃/(I/I₃)/Pt. The photovoltaic performance was measured under standard one sun conditions as presented in Fig. 2(a). The champion solar cell produced V_{oc}, J_{sc}, FF and PCE of 0.137 V, 5.95 mA cm⁻², 43% and 0.35%, respectively. Meanwhile, the corresponding average performance of several devices prepared under similar condition is 0.129

V, 4.82 mA cm², 45% and 0.27%. Apparently, the present result (CuO-based PSCs) is better than other p-type liquid-state DSSCs based on CuO photocathode as reported in previous studies. For example, Sumikura et al. [6] and Langmar et al. [7] acquired merely 0.01% and 0.10% PCE, respectively, which is majorly due to low J_{sc} value (<3 mA cm²). The improved performance of our device could be attributed to the remarkable improvement of light absorption when CH₃NH₃PbI₃ layer was fabricated using our developed technique. To further investigate the source of the photocurrent, an identical cell was made without CH₃NH₃PbI₃ layer and the cell behaviour under light illumination and dark condition is presented in Fig. 2(b). It is obvious that the J_{sc} and V_{oc} produced in the absence of perovskite layer approached zero confirming that the perovskite layer is the key parameter in improving the PCE parameters of our cell.

Fig 2(c) displays the incident photon-to-electricity conversion efficiency (IPCE) spectrum which was used to determine the external quantum efficiency (EQE) of the cells. The IPCE spectrum increased steadily from the UV region to near IR before starting to decrease at around 760 nm, which matched well with the bandgap of perovskite determined from UV-Vis analysis. The wavelength dependent photocurrents were integrated to calculate the photocurrent of the solar cell. The integrated J_{sc} is 6.58 mA cm² which is in a good agreement with the value obtained from the J-V curve. It is worth mentioning that the device lifetime is rather short (<10 min) because CH₃NH₃PbI₃ rapidly dissolves in the redox electrolyte. Therefore, further device optimization is still underway for improving the efficiency and stabilizing the performance. However, the present work suggests that the two-step hot-air drying method developed in this work is practicable for preparing a functional perovskite sensitizer and advantageous in terms of rapid fabrication process.

The effect of changing light intensity on liquid-state CuO PSCs was also studied and the corresponding photovoltaic parameters are presented in Fig. 3(a)-(e). Linear increase in J_{sc} and V_{oc} was observed upon increasing the incident photon concentration. Such behaviour could be attributed to the enhanced excitation of electron-hole pairs and less charge recombination under intensified light illumination. Meanwhile, FF value experienced slight drop as the light intensity increased which ultimately affected the over-all device efficiency. Despite the decrease of efficiency, this analysis actually implies that our liquid-state CuO-based PSCs are more effective for indoor light harvesting or generation of electrical power during cloudy conditions.

Fig. 1. (a) XRD patterns and (b) absorption spectra of CuO before and after being sensitized with CH₃NH₃PbI₃. (c) FESEM image of perovskite layer grown on FTO-coated CuO by hot-air drying method.

Fig. 2. (a) Photovoltaic performance of a complete cell FTO/CuO/CH₃NH₃PbI₃/(I⁻/I₃⁻)/Pt. (b) Photovoltaic performance in the absence of the perovskite layer FTO/CuO/(I⁻/I₃⁻)/Pt. (c) The IPCE of FTO/CuO/CH₃NH₃PbI₃/(I⁻/I₃⁻)/Pt.

Fig. 3. (a) J-V curves and the corresponding (b) V_{OC}, (c) J_{SC}, (d) FF and (e) PCE of the liquid-state electrodeposited CuO-based PSCs under different light intensity.

4. Conclusion

We have developed a facile and rapid method for making CH₃-NH₃PbI₃ layer through hot-air drying process and successfully applied it for sensitising CuO electrodes. This process consumed less than 10 min for complete assembly of the liquid-state CuO-based PSCs. The cell efficiency achieved 0.35% which could be due to the effective light absorption by perovskite material and the compatibility between CuO and perovskite as photocathode and sensitizer, respectively. We believe that this work will help advancing the solar cell technology towards the development of liquid-state tandem solar cells with reduced fabrication time and cost.

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