



Fabricating the solution-processable inverted photovoltaic devices by the dip-coating method



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ABSTRACT

All solution processable photovoltaic (PV) devices have been great interests in the past decade and different processing methods have been explored to produce the PV devices. In this paper, the dip-coating method was studied to fabricate core layers in the inverted polymer photovoltaic devices, which demonstrates that the dip-coating technology has its potential to produce large area PV devices. The crystallinity of the active layers by the dip-coating method can be improved under the condition of the extended drying rate. Light absorption spectra and X-ray diffraction (XRD) patterns of the active layers were investigated to confirm the improved crystallinity of the active layers. Various morphologies of the dip-coated layers were observed by the atomic force microscopy (AFM). The best PV device achieved ~3.4% power conversion efficiency.

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1. Introduction

The solution-processable photovoltaic devices (SPPDs) mainly including dye-sensitized TiO₂ [1], quantum-dot nanoparticles [2], organic semiconducting polymers [3], and very recent perovskites [4] represent great opportunities and advantages of easy fabrication, cost effectiveness, devices on flexible substrates, and large area devices by the roll to roll (R2R) [5–7] or other simple solution manufacturing methods [8]. The solution-processed methods may be classified as spin-coating, spray-coating, dip-coating, doctor-blading, screen (or ink-jet) printing methods, etc. [9,10]. The spin coating is one of the most efficacious techniques and has been widely used in laboratories for fabrication of SPPDs due to its advantages of easy use and high-degree regularity for the forming film. Fabrication of SPPDs in most published papers has used the spin-coating method. Nevertheless, there is a limitation for the spin-coating method because it is only suitable

for small-scale fabrication or small area devices, not being compatible to the commercial applications for large-scale devices. Other methods have their advantages and drawbacks. The spray-coating method needs precisely control on the nozzles and the liquid droplets may splash to the previously coated areas affecting the properties of the photovoltaic (PV) devices. The doctor-blading or the printing methods can easily realise the R2R manufacturing of PV devices. However, their disadvantages could include complicated chemistry of ink formulations and contact effects when the latter layer is applied on the previously formed film. The dip coating method has its own features and potential to be used as a promising alternative for fabricating large area SPPDs in industrial scale. Historically, the dip-coating process is a very old technology of producing sol-gel thin films, which was invented by Jenaer Glaswerk Schott & Gen. in 1939 for silica films [11]. A schematic diagram is shown in Fig. 1 for the dip-coating process. The substrate is pulled vertically from the coating bath at a constant speed V_p . The entrained liquid by the moving substrate splits into two at the free surface (point S in Fig. 1) in a viscous boundary layer, returning the outer layer to the

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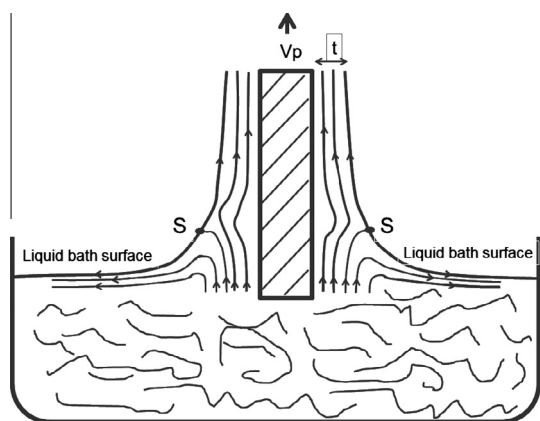


Fig. 1. Schematic diagram of the dip-coating technology.

bath. When the upward moving flux is balanced above the stagnation point *S* due to evaporation of the solvents, a continuing and position-stable film is formed with respect to the coating bath surface. Within the drying process, the colloids are progressively concentrated by evaporation, leading to aggregation, gelation, and final drying to form a type of a dry gel or xerogel film. When the substrates' speed (V_p) and liquid viscosity (η) are low, e.g. in the case of the sol-gel coating, the thickness of the wet film can be written as:

$$t = [0.94(n * V_p)^{2/3}] / [\gamma_s^{1/6}(\rho * g)^{1/2}] \quad (1)$$

where γ_s is the liquid-vapour surface tension, ρ is the liquid density and g is the acceleration of gravity [12]. Dip-coating process is a simply high productivity technique with a high accuracy to deposit a uniform film on a large scale area. Nowadays, many commercial optical functional sol-gel thin films on glass have been manufactured by the dip-coating method with a large area of several square metres. Moreover, the dip-coating method owns the advantages of significantly reducing the amount of wasted materials during the processing and the potential capability of depositing two PV devices at the same time.

Polymer photovoltaic devices (PPVs) have attracted considerable interests in the last decade due to their potential advantages of the solution-processable manufacturing. Power conversion efficiency (PCE) has increased after bulk heterojunction (BHJ) structures were introduced in the devices [13], where the donor (organic polymers) blends together with the acceptor (fullerene derivatives) in a thin combined film placed between the electron transport layer (ETL) and the hole transport layer (HTL) that are connected to the electrode layers separately. Recently, ~8% PCE has been achieved in a single BHJ device using the new low band gap material [14–17]. Although these significant achievements have pushed the technology of PPVs further towards the application of commercial products, there are still huge challenges to be overcome with much effort including large area high-PCE devices and long-term stability of the devices.

Dabirian et al. investigated the properties of the dip-coated PCBM [18]. Xue et al. produced bundles of

P3HT nanorods by using the dip-coating method [19]. Hu et al. has published a study to deposit the active layer of PPV devices in the conventionally structural devices [20]. In this paper, we report the deposition of all layers except the electrodes in the inverted PPVs by the dip-coating technology. We modified our blend of the active layer based on the chlorobenzene-dispersed P3HT:PCBM and transformed it into a sol-gel-like solution by adding a long-chain hydrocarbon containing solvent. Fig. 2 shows a gel of the P3HT:PCBM blend with high concentration of the long-chain hydrocarbon containing solvent after stored in a closed bottle in the glovebox for two days. The blend can also form a gel much faster with evaporation of chlorobenzene than that it is stored in the closed environment, which is compatible for the use of the dip-coating process in order to fabricate a uniform active layer for PPV devices. We also used the dip-coating method to produce the ETL and HTL layers. Efficient devices with the PCE around 3.4% were obtained. This exploration demonstrates that the dip-coating method has its own potential and advantages to be used as an industrial scale method for fabrication of all layers of SPPDs.



Fig. 2. Photos of the P3HT:PCBM blend: (left) A gel formed from the modified blend; (right) the liquid blend of the unmodified P3HT:PCBM in chlorobenzene.

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