Spray deposition of electrohydrodynamically atomized polymer mixture for active layer fabrication in organic photovoltaics

Sung-Eun Park, Jun-Young Hwang, Kangmin Kim, Buyoung Jung, Woochul Kim, Jungho Hwang*

School of Mechanical Engineering, Yonsei University, 262 Seongsanno, Seodaemun-gu, Seoul 120-749, Republic of Korea

ABSTRACT

Printing and spray technologies are the most recent and novel approaches to form organic photovoltaics (OPV) with inexpensive, high speed, and environmentally friendly process. With an electrohydrodynamic atomization (EHDA) approach, the active layer composed of polymer mixture (P3HT:PCBM) was successively fabricated. Operating conditions for obtaining the stable cone jet mode were determined with various applied voltages and liquid feed flow rates. The size distribution of EHDA droplets was characterized by aerodynamic particle sizer (APS) measurement. The mode diameters of the droplets were 580 and 670 nm, respectively, when the liquid flow rates were 1 and 20 μl/min. The maximum power conversion efficiency of 0.48% was obtained under AM 1.5 solar simulation for an OPV device fabricated in air.

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1. Introduction

Recent developments in photovoltaics have been focused on the cost-effective and mass-productive photovoltaics. For the fabrication of organic photovoltaics (OPV), the spin coating process has been widely used. In the spin coating process, however, large material consumption, low production rate, and consequently high production cost are involved. Therefore, various fabrication techniques of organic materials such as doctor blading, roll-to-roll (R2R), spray deposition, and inkjet printing are applied recently [1]. These fabrication techniques are characterized by large areal processing and continuous process, and offer the solution to the problem of high cost for photovoltaic technologies for the next step to real production.

The usage of the deposition methods has been focused on the formation of transparent electrode of poly(3,4-ethylenedioxythio-phene)/polystyrene sulfo-nate (PEDOT/PSS), which is used as a buffer layer between the active layer and indium tin oxide (ITO) electrode. Eom et al. [2] reported the inkjet-printed PEDOT/PSS layer based polymer solar cell and its device performance. Steirer et al. [3] demonstrated that the PEDOT/PSS electrode was ultrasonically spray deposited or inkjet deposited without significant losses to the film. There were several attempts to fabricate the active layer consisting of organic materials in the organic photovoltaics. Schilinsky et al. [4] reported that the power conversion efficiency was 4% in solar cells of which active layer

was prepared by doctor blading. Hoth et al. [5] made the bulk heterojunction type organic photovoltaics using spray coating and reported an efficiency of 3.1%. Green et al. [6] used air-brush spray deposition for the preparation of active layers with efficiencies of over 2%.

Electrohydrodynamic atomization (EHDA) process, also referred to as electrospray process, is the most recent approach to generate fine particles whose diameters range from micro to nanoscales with a narrow size distribution. In the EHDA process, highly charged, relatively monodisperse droplets of controlled size can be produced from various conditions of liquid solution material [7–10]. To maintain droplet monodispersity, the atomization must be operated in the cone jet mode of electrospray [11–13], where axisymmetric surface wave instabilities dominate the liquid jet break-up, resulting in a constant ratio of 1.89 between the primary droplet diameter and the jet diameter [9]. In the EHDA process, since the diameter of the nozzle ($>100\,\mu m$) is much larger than that used in inkjet printing (about 20 μm), nozzle blockages are prevented.

Many researchers studied the particle generation via EHDA and produced the nanoparticles composed of organic materials. The sizes of the particles depended on many parameters including liquid flow rate, ink property, and applied voltage. Hogan et al. [8] demonstrated that water soluble and water insoluble, low dispersity polymer particles could be readily prepared by EHDA with geometric mean diameters in the 0.35–2.71 μm size range. Yao et al. [10] introduced fabrication of 1 μm sized polymeric particles in a modified EHDA system. They used organic liquid polylactide co-glycolic acid (PLGA) and suggested an empirical equation for the droplet size .

In this paper, we produced monodispersed polymer droplets using EHDA spray deposition method and fabricated lab-scale OPV. A high-speed camera was employed for monitoring the deposition process and the droplet size distribution was measured using an aerodynamic particle sizer (APS). The morphology of the prepared active layers was investigated by a surface profiler as well as by an optical microscope. The electrical characteristics of the active layers were estimated by a source-meter and a solar simulator.

2. Experimental

2.1. Materials

The polymeric solution containing a mixture of regioregular poly(3-hexylthiophene) (P3HT), purchased from Rieke Metals, and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61 (PCBM), purchased from Nanocraft Inc., was prepared for EHDA. Both P3HT and PCBM were dissolved in chlorobenzene, at a ratio of 1:1.

2.2. Experimental setup

The polymer nanoparticles were generated by the EHDA system, which was similar to those used previously for micro-patterning of solutions based on conductive metals and ceramics [14–16].

The experimental setup consisted of a liquid supply system, a moving stage system, an electrical system, and a visualization system. The liquid supply system included a syringe pump, a feeding tube, and a stainless steel nozzle (inner diameter: 150 μm, outer diameter: 300 μm). The moving stage system consisted of an X–Y stage and a motor controller with a driver. The electrical system consisted of a high voltage power supply ($\sim$DC 15 kV) and two electrodes. The pin-type nozzle used for the liquid supply system was also used as the anode. The ring-type copper electrode (1 mm in thickness and 11 mm in diameter) located 5 mm below the nozzle and 50 mm above the substrate was used as the ground electrode. High speed images were taken with a visualization system consisting of a high speed camera (Motion Pro HS-4, Redlake Inc.). This camera was capable of capturing 5130 frames/s when the images were fixed at a 512×512 pixel resolution. The exposure time was fixed to 10 μs in all captures.

The electrohydrodynamically generated droplets were sampled into an APS measurement system. The APS (Model 3321, TSI Inc.) is used to determine the concentration and size distribution of particles from 0.5 to 20 μm in an aerodynamic diameter at concentrations up to 1000 particles/cm^3. This instrument sizes particles aerodynamically by a time-of-flight and/or optically by light scattering intensity. The aerodynamic diameter d_a is the diameter of the unit density ($\rho_0 = 1$ g/cm^3) sphere that has the same settling velocity as the particle of diameter d_d (Stokes diameter). The relationship between the Stokes diameter and the aerodynamic diameter is

$$d_d = d_a \times \left(\frac{\rho_0}{\rho_d}\right)^{1/2} \left(\frac{C_c(d_a)}{C_c(d_d)}\right)^{1/2} \tag{1}$$

where ρ_d is the droplet density. $C_c(d_d)$ and $C_c(d_a)$ are the slip correction factors for droplet diameter (Stokes diameter) and aerodynamic diameter, respectively. To minimize the penetration of ambient aerosol particles into the experimental setup, all experiments were conducted in a class 100 (above 0.5 μm) clean room. All experiments were repeated three times and the results of measurements were averaged.

The active layer of a P3HT and PCBM mixture was deposited onto a substrate (glass slide: 4 cm $\times$ 4 cm) having two ITO line patterns (each line: 8 mm $\times$ 4 cm, thickness $\sim$100 nm). Before the deposition process, the substrate was cleaned via sonication in detergent, DI water, acetone, and finally isopropyl alcohol, and a conducting polymer of PEDOT/PSS layer was spin coated. After the EHDA deposition process, the substrate was dried at the temperature of 140 °C for 20 min and cooled to room temperature. Finally, the sample was transferred in a thermal evaporator for metal electrode (Al) deposition at the pressure of 2×10^{-6} Torr. The deposition rate was 2 Å/s. The pattern width, length, and thickness were 8, 4 cm, and around 100 nm, respectively. The active area of the fabricated device was 64 mm^2. The surface

Table 1
Operating range of different modes with applied voltage and flow rate.

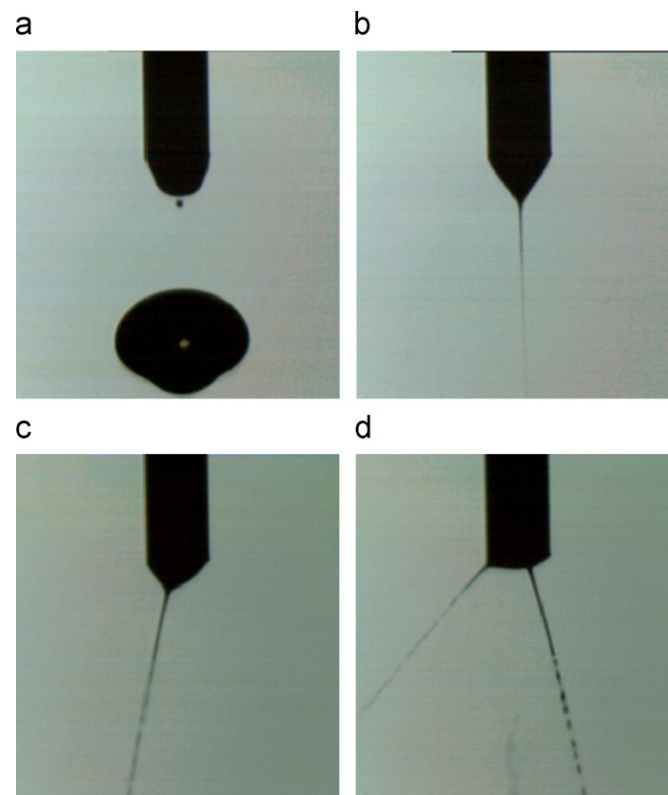| Flow rate	~3 kV	4 kV	5 kV	6 kV	7 kV	8 kV	9 kV
1 μl/min	Dripping		Pulsating cone jet		Stable cone jet	Multi jet	
5 μl/min	Dripping		Pulsating cone jet		Stable cone jet	Multi jet	
20 μl/min	Dripping			Pulsating cone jet	Stable cone jet		Multi jet

Fig. 1. Shapes of meniscus and jet break-up to the atomization: (a) dripping (b) pulsating cone jet (c) stable cone jet, and (d) multi-jet.