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Roll-to-roll printing of flexible thin-film organic thermoelectric devices

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Abstract

This paper presents a continuous process for printing flexible thin-film thermoelectric devices via a roll-to-roll (R2R) system. Poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS) was used as inks for printing *p*-type strips and connection strips. Nitrogen-doped graphene was dispersed into solvents to serve as *n*-type inks for printing *n*-type strips. The substrate and roller surfaces were treated for desired ink-wettability. With tunable rotation pressure and speed, the inks were transferred and printed to the flexible plastic films for horizontal thermoelectric devices. At a temperature gradient of 10 °C, the thin-film thermoelectric devices could generate an electric power of ~0.24 mW/m^2 and the maximum voltage reached 3 mV, indicating great potentials for practical applications.

Keywords: Roll-to-roll; Thermoelectric; Printing; Flexible

1. Introduction

Thermoelectric energy conversion is based on the Seebeck effect and allows for the generation of electricity directly from a supply of thermal energy. The conversion efficiency is governed by the thermoelectric figure of merit (ZT), $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature at operation [1,2]. The ZT value directly affects the efficiency of thermoelectric conversion, i.e., larger ZT means higher efficiency. Recent advances in material science provide a path to achieve high ZT values by coordinating the conflicts among S, σ and κ. Tailoring the material structures is considered an effective approach to facilitate independent control of Seebeck coefficient and electrical conductivity [3–6].

Within the last years, a progressive improvement in the ZT value at room temperature has been demonstrated from 0.01 to ~0.4 by creatively synthesizing new organic thermoelectric materials and employing specific structures [1–7]. In 2011, Crispin's group showed that PEDOT optimized with tosylate dopants can provide a ZT value of 0.25 [5]. In 2013, Pipe's group further optimized the poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS) morphology for improved mobility, and achieved further increase in ZT value at room temperature [6]. In 2014, the Chabinyc's group demonstrated outstanding performance for the *n*-type polymer [7]. Such organic thermoelectric materials demonstrate outstanding properties and hold significant promise for developing flexible and affordable thermoelectric devices for power generation. In additional, inorganic nanoparticle-filled polymer composites also demonstrate outstanding thermoelectrics. For example, Bi_2Te_3/polymer composite demonstrate $ZT \sim 0.2$ [8,9].

A single thermoelectric material can generate slight voltage due to the temperature gradient. Electrons diffuse from the hotter region of the material toward the colder region and consequently build up a small voltage between two

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ends of the material [10–12]. Usually, the generated voltage is <50 μV for organic materials. If two dissimilar *p*- and *n*-type thermoelectric materials are connected in series and thermally in parallel, a larger voltage can be developed to supply electric power (for example, output voltage is above 1 mV for organic thermoelectric devices). A single-module thermoelectric device only consists of one *p*-type element and one *n*-type element while multiple modules-based thermoelectric devices consist of many *p*-type and *n*-type elements [13–16]. The power generation is significantly dependent on the number of modules and the temperature gradient.

Lithography is a typical method for manufacturing of inorganic thermoelectric devices [17–19]. However, it is challenging to transfer patterns onto flexible and costly substrates such as polymer films with conventional lithography technology. The difficulty of thoroughly removing solvent residuals on both patterned and un-patterned areas may become a potential corrosive source for final products, making it infeasible for organic thermoelectric devices [19]. Thermal evaporation and sputtering are also used for the thermoelectric device fabrication, but in very small sizes and low yield [20,21]. Recently, inkjet printing is attempted to fabricate thin film thermoelectric devices, which is a low cost, solution-based, localized digital deposition process without wastage of materials and masks [22,23]. However, it provides relatively low throughput and involves time-consuming post treatments due to ink bleeding and liquid blurring [14]. Screen-printing has also been used to create versatile patterns [24,25] without requiring high pressure or planar substrates. Various inks can be employed to work with a variety of materials, such as paper, metal and plastic. However, screen-printing technique is generally only applicable for high-viscosity inks with shear-thinning behavior, as inks with lower viscosities will simply run through the mesh [26,27]. Current high-performance organic thermoelectric materials-based inks, such as PEDOT: PSS colloids usually show very low viscosity.

Roll-to-roll (R2R) printing has been actively investigated for manufacturing of various electronic devices [28–33]. Gravure based R2R printing is a popular printing technology for organic photovoltaic devices by engraving the desired image onto a patterning stamp on a rotary roller and then the ink is transferred to the substrate. The doctor blade scrapes the cylinder before it makes contact with the substrate, removing excess ink from non-printing areas and leaving the right amount of ink in the cells. Usually, large-area flexible devices (including electronics embedded in clothing, large flexible displays, etc.) composed of thin-film transistors can be easily patterned by those R2R printing methods. The size can be scaled up to a few meters wide and 50 km long at a fraction of the cost of traditional semiconductor manufacturing methods. Krebs et al. [34] combined the Flexo printing and rotary screen printing to fabricate three-layered structures (Ag layer/PEDOT:PSS layer/Ag layer) for thermoelectric conversion, but no attempt has been found in continuous manufacturing typical *p*-*n* junctions based thermoelectric devices.

In this paper, we innovatively demonstrate the continuously R2R manufacturing of large-area flexible thermoelectric devices which include both *p*- and *n*-type elements as horizontal junctions.

2. Experimental

2.1. Material

Nitrogen-doped graphene powder (NG, conductivity: 1000 S/m. Lateral size: 0.5–5 um. Nitrogen: 3.0–5.0 at%) was purchased from ACS material. PEDOT/PSS (poly(3, 4-ethylenedioxyhiophene)-poly(styrenesulfonate), Clevios™ PH 1000. Solid content: 1.0–1.3%. Specific conductivity: 850 S/cm. Viscosity: 15–50 mPa s) was obtained from Heraeus. DMSO (dimethyl sulfoxide), polyethylene film, and EG (ethylene glycol) was bought from Sigma Aldrich.

2.2. Ink preparation

The PEDOT ink was prepared by adding 5% of the DMSO into 15 ml PH 1000 and named as PEDOT ink. The nitrogen-doped graphene ink was prepared by sonication of nitrogen-doped graphene into EG to form 0.1 mg/ml solution and named as graphene ink. The dispersion of these two inks is stable for at least 12 h.

2.3. Printing process

An in-house built R2R system was used for the continuous printing thin-film thermoelectrics. As-built R2R system consists of three sequential rollers for transferring inks to the web with desired patterns. The ink is kept in the epoxy-coated reservoir. An ink transfer cylinder is halfway emerged in the reservoir help to transfer inks from the reservoir. As the ink transfer cylinder rotates, the inks could get in contact with the extruded features of the printing cylinder, and thus is transferred onto the features of the printing rollers. As the printing roller rotates and contacts substrate, the substrate (web) is pressed in between the printing cylinder and the impression cylinder, and the ink will transfer onto the bottom of the web. The web could be propelled through the system by friction and as it passes each plate cylinder it will produce the patterns on the web. The web speed is around 15–20 mm/min.

2.4. Characterization

The morphology of the *n*-doped graphene was investigated by the transmission electron microscope (TEM, T8100, HITACHI) and scanning electron microscope (SEM, HITACHI S4300). For the power-generation tests, an AC electrical heater was applied on one side of the thermoelectric devices while the other side stayed cool, and