

# Influence of doped PEDOT:PSS on the performance of polymer solar cells

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## ABSTRACT

The influence of anode buffer layers of doped poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) on the performance of solar cells made from blends of poly(3-hexylthiophene) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester has been investigated. Different concentration of ethylene glycol were added into the PEDOT:PSS solution to increase its conductivity. The surface roughness of the doped PEDOT:PSS film was changed, which was examined by atomic force microscopy. The best doped device with a power conversion efficiency of 4.39% as compared to 3.41% for the pristine device has been achieved. The enhanced PEDOT:PSS conductivity improved the short circuit current and fill factor of the doped device. The almost constant open circuit voltage indicated the well-established ohmic contact between the anode and active layer irrespective of the doping of the PEDOT:PSS. The changed surface roughness of the doped PEDOT:PSS film did not correlate with the morphology of the consequent active layer and the resultant device performance.

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## 1. Introduction

Organic photovoltaic devices (OPVs) have attracted considerable attention due to their potential for flexible, lightweight, and low-cost applications of solar energy conversion [1–3]. Since the first report of organic solar cell based on blends of conjugated polymer and fullerene derivative, device performance has been greatly improved by selection of material with suitable energy level, optimization of electrode material, and control of nanomorphology using post-fabrication procedure such as thermal annealing and solvent annealing [4–7]. Devices composed of the widely studied poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) have been reported to produce power conversion efficiency (PCE) of 4–5% [4–6].

Most of these high efficiency polymer:fullerene solar cells include a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer, which is inserted between the transparent electrode, typically indium-tin oxide (ITO) and the light-absorbing organic layer [4–8]. The advantages of incorporating PEDOT:PSS buffer layers in OPVs stem from several properties that are closely related to its beneficial use in organic light-emitting diode [9,10], even the PEDOT:PSS film associates with some stability problems [11]. The positive effect of this PEDOT:PSS layer on device performance has been attributed to improved selectivity of the anode, on account of the higher work function relative to ITO, improved smoothness of the

electrode/active layer contact, and facilitated hole transportation [12–15]. However, the increased series resistance of OPVs is unavoidable due to the introduction of PEDOT:PSS layer. It is well known that the conductivity of the doped PEDOT:PSS can increase greatly over two orders of magnitude after the doping with polar solvents [16–18]. The effect of organic solvents on the PEDOT:PSS film has been investigated by different methods [19–22]. Furthermore, the effect of the PEDOT:PSS film on the performance of OPVs also has been studied by varying its thickness, thermal annealing temperature, UV light-irradiation, and reducing its acidity [23–26]. However, the influence of the conductivity and morphology of the doped PEDOT:PSS on the OPV performance has not been fully understood. Zhang et al. found that the short-circuit current ( $J_{sc}$ ) of OPV increased with the high conductivity of the PEDOT:PSS buffer layer, but the open-circuit voltage ( $V_{oc}$ ), the fill factor (FF) and resulting PCE decreased [27]. Ko et al. confirmed that the device improvement was due to the reduction of series resistance of the PEDOT:PSS layer after the mannitol doping [28]. However, Xiao et al. claimed that the improved cell performance was possibly due to improved light scattering by the rougher surfaces of PEDOT:PSS that results in enhanced absorption in the active layer, and the changes in the PEDOT:PSS conductivity did not correlate with the improved performance [29]. Therefore, the influence of the doped PEDOT:PSS on the performance of polymer solar cells are only partly understood and subject of further study.

In this study, a highly conductive PEDOT:PSS film, obtained by addition of a polar solvent, ethylene glycol (EG), to an aqueous solution of PEDOT:PSS, was investigated. The changed conductivity and morphology resulted from the addition of various amounts of

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EG were observed. Significantly, we examined the use of the doped PEDOT:PSS film as a buffer layer to achieve high-efficiency OPVs based on P3HT and PCBM. The enhanced PEDOT:PSS conductivity improved the  $J_{sc}$  and FF of solar cell. The almost constant  $V_{oc}$  indicated the well-established ohmic contact between the anode and active layer irrespective of the doped PEDOT:PSS. The changed surface roughness of the doped PEDOT:PSS did not correlate with the morphology of the consequent active layer and the resultant device performance.

## 2. Experimental

A commercially available aqueous PEDOT:PSS dispersion (Baytron P VP Al 4083 from H.C. Starck) has been used. Different amounts of EG (5%, 10%, 15%, 20% or 25%) were added to the aqueous dispersion. The solution was stirred for at least 24 h at room temperature, filtered using a 0.45  $\mu\text{m}$  filter, and deposited in air by spin coating, which formed a thick film (40–50 nm). For comparison, we used PEDOT:PSS without EG referred to as pristine. To fabricate OPVs, PEDOT:PSS was firstly spin-coated

on the cleaned ITO ( $R_s = 10 \Omega \text{sq}^{-1}$ ). After annealing the PEDOT:PSS film at 150 °C for 30 min in air, the active layer P3HT (Rieke Metals, 90–93% regioregular) and PCBM (Nano-C, 99%) with the weight ratio of 1:0.8 were then spin-coated from chlorobenzene to form about 200 nm thin film. The prepared organic film was then treated following the so-called solvent annealing procedure as described in the Ref. [6]. Finally, a LiF/Al (1/80 nm) electrode was deposited via thermal evaporation as the cathode. More than eight cells were fabricated for each doped buffer layer with the active area of 0.08  $\text{cm}^2$  defined by shade mask. Device current density–voltage ( $J$ – $V$ ) characteristics were measured using a Keithley 2420 under 100  $\text{mW}/\text{cm}^2$  simulated AM 1.5 G solar illumination (Oriel 96000, 150 W). The intensity of the lamp was calibrated using a Si photodetector (without a standard compensation for the spectral mismatch). The surface morphology of the PEDOT:PSS layers was measured by atomic force microscope.

## 3. Results and discussion

First, we investigated the effects of the amount of added solvent on the electrical properties of the films. Fig. 1 shows the conductivities of PEDOT:PSS films that had been modified with various amounts of EG. The conductivity of each PEDOT:PSS film was evaluated using four-point-probe measurements. As shown in Fig. 1, the conductivity of doped PEDOT:PSS increased greatly, which is more than two orders of magnitude greater than that of the pristine. In particular, the conductivity firstly increased with the addition of EG and then decreased. The conductivity of the film reached the maximum at the doping of 10%.

In fact, the enhancement of PEDOT:PSS film conductivity by addition of high-boiling solvents and polar compounds is well-known and has been widely studied [16–22]. Herein, the morphology of PEDOT:PSS solid films after drying was recorded to investigate possible changes in morphology. Fig. 2 shows the atomic force microscopy (AFM) topography of PEDOT:PSS films modified by the addition of various amounts of EG. Sample preparation for AFM measurements (Fig. 2) was identical to that used for the conductivity measurement shown in Fig. 1. Fig. 2(a–f) presents the topography images of a  $1 \times 1 \mu\text{m}^2$  area of the doped

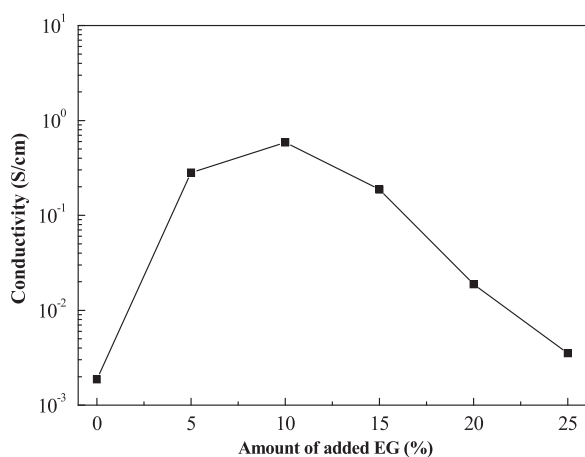


Fig. 1. Conductivity of PEDOT:PSS films prepared using different amounts of added EG and annealing at 150 °C for 30 min.

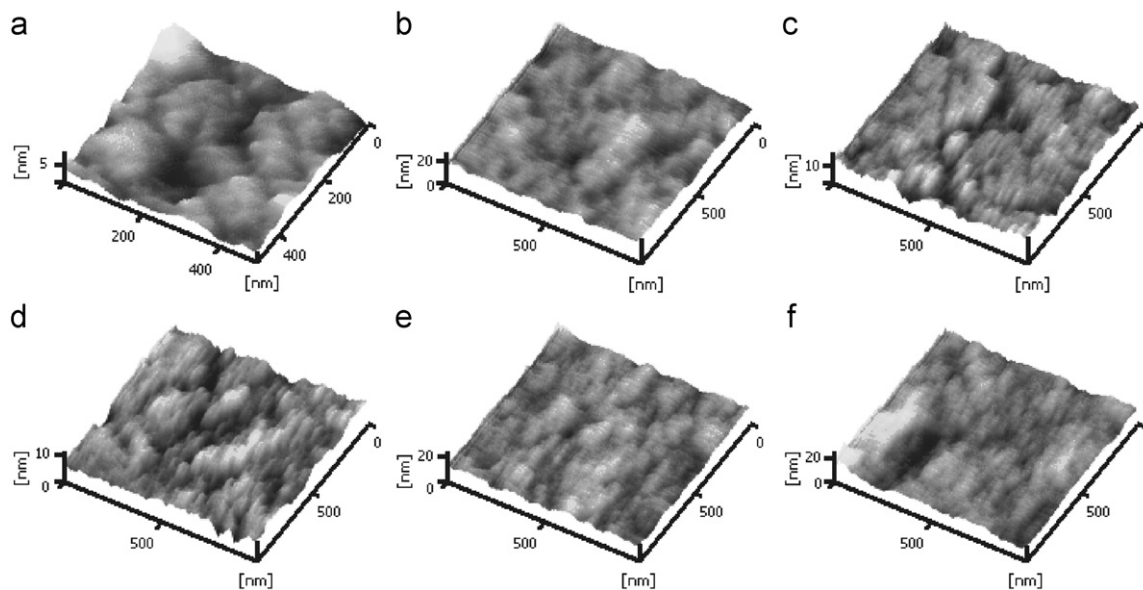


Fig. 2. AFM topography (a–f) of PEDOT:PSS films modified with various amounts of added EG: (a) 0%; (b) 5%; (c) 10%; (d) 15%; (e) 20%; and (f) 25%. All images captured an area of  $1 \times 1 \mu\text{m}^2$ .

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