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A nonionic surfactant simultaneously enhancing wetting property and electrical conductivity of PEDOT:PSS for vacuum-free organic solar cells

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ABSTRACT

In this work, we report a nonionic surfactant (polyethylene glycol 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol ether, PEG-TmDD) that can improve the wetting property of PEDOT:PSS aqueous solution on the organic photoactive layer and *simultaneously* enhance the electrical conductivity of PEDOT:PSS film up to 526 S/cm. Furthermore, the conductivity enhancement is significantly dependent on the thermal annealing, which is contrary to the conductivity behavior of PEDOT:PSS film prepared from the formulation added with ethylene glycol (EG) where the conductivity is almost independent of the thermal annealing. The temperature dependence of the conductivity of PEDOT:PSS by PEG-TmDD is possibly ascribed to decomposition of PEG-TmDD into EG and TmDD during thermal annealing. With the high conductivity and good wetting on the active layer, PEDOT:PSS mixed with PEG-TmDD is used as the top electrode for organic solar cells. The cells exhibit a fill factor of 60% and a power conversion efficiency of 4.1% using poly(3-hexylthiophene):indene-C60 bis-adduct as the active layer. The results indicate that the new formulation of PEDOT:PSS mixed with PEG-TmDD is suitable for preparing a top electrode for vacuum-free organic solar cells.

1. Introduction

Conducting polymers have been attracting great interests because of their tunable conductivity, ease of processing and good mechanical flexibility. Poly (3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, Fig. 1a) is the most studied conducting polymer [1–9]. PEDOT:PSS films can be readily prepared through a solution-processing technique such as spin coating, ink-jet printing [10], or roll-to-roll coating [11]. It has been used for broad applications, such as antistatic applications, printed wiring boards and so on. In addition, due to its high work function of 4.8–5.0 eV [7,12,13], PEDOT:PSS has been widely used to facilitate the hole injection or collection in organic or hybrid electronic devices [7,14].

Not only as a hole injection or collection layer, the PEDOT:PSS itself is also expected to be an excellent candidate as a transparent electrode to replace brittle and expensive indium tin oxide (ITO) transparent electrode because the electrical conductivity of PEDOT:PSS has been significantly enhanced recently. Two different types of methods have been found that could enhance the conductivity effectively. One is by adding additives into the PEDOT:PSS aqueous solution, such as dimethyl sulfoxide (DMSO) [13,15–21], ethylene glycol (EG) [22–25], D-sobital [26–28], or ionic liquids [29,30]. The other effective method is via a post-treatment on the PEDOT:PSS film to enhance the conductivity. Post-treatment of EG [23], salts [31,32], DMSO [33–35], methanol [36], glycerol monostearate [37], hexafluoroacetone [38], or acids [39–42] could significantly enhance the conductivity of PEDOT:PSS. With these methods, several groups have reported that the conductivity of PEDOT:PSS could reach above 1000 S/cm [23,29,35–40]. Especially a conductivity of above 3000 S/cm has been reported by post-treatment on the PEDOT:PSS (PH1000 formulation) using sulfuric acid, which is close to that of ITO [39,40]. The solar cells with the treated PEDOT:PSS as the bottom electrodes show comparable power conversion efficiency to the reference cells with ITO as the bottom electrodes. The sulfuric treatment is harsh. It is not suitable for the electrodes deposited on top of the organic active layers.

Inverted organic solar cells that use high-work function electrodes as the top electrodes to collect holes show good air stability and become more and more popular because there is no need of air-sensitive low-work function metals in this structure.

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Commercially available PEDOT:PSS that has a high work function of about 5.0 eV could be used as the top electrode for hole collection. The use of solution-processed PEDOT:PSS as the top electrode to replace high-vacuum deposited metal electrodes will simplify the device fabrication [12,43]. The wetting of the PEDOT:PSS aqueous solution on top of the active layer is typically poor. Fig. 1c shows that the contact angle of commercially available PEDOT:PSS solution (PH1000 formulation, hereafter referred to as PH1000) on top of thermally annealed poly(3-hexylthiophene):indene-C60 bis-adduct (P3HT:ICBA) is about 90°. To deposit uniform PEDOT:PSS film on top of the hydrophobic surface of the active layer, one way is to tune the surface of active layer hydrophilic by a mild air or oxygen plasma treatment; the other way is to add surfactant into the PEDOT:PSS aqueous solution. Surfactants such as Zonyl® series and Dynol® series have been commonly added into the PEDOT:PSS aqueous solution to enhance the wetting properties. Another type of PEDOT:PSS formulation that is widely used for antistatic coating PEDOT:PSS CPP series containing 0.1–0.3% of Dynol® 604 surfactant has good wetting property on top of the hydrophobic surface [44]. As shown in Fig. 1c, the addition of 0.4 wt% polyethylene glycol 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol ether (PEG-TmDD, Fig. 1b, the main component of Dynol® 604 or 607, TOYNOL® Superwet-320 or 340) decreases the contact angle of PH1000 solution on the photoactive layer to about 30°. While the surfactant has been widely used to improve the wetting property of PEDOT:PSS aqueous solution, there are few reports on these nonionic surfactants that can significantly enhance the conductivity of these films. Ouyang et al. reported that adding of a nonionic surfactant polyoxyethylene(12) tridecyl ether obtained limited conductivity enhancement of PEDOT:PSS (Baytron P), from 0.16 to about 3 S/cm [45]. Recently Oh et al. reported that Triton X-100 could enhance the conductivity of PEDOT:PSS to about 100 S/cm [46]. The PEG-TmDD is commonly used as the surfactant for wetting enhancement of aqueous solutions. People usually ignore the fact that the conductivity of PEDOT:PSS which can be enhanced by PEG-TmDD. However, conductivity is very important when the layer is used as the interlayer for both single-junction and tandem organic solar cells. The devices will show large leakage current if the high conductivity is not noticed and the highly conductive interlayer is not properly patterned.

In this work, we report that the PEG-TmDD could enhance the conductivity of PEDOT:PSS to 526 S/cm at a relatively higher concentration of 4 wt%. The enhancement of conductivity is strongly dependent on the annealing temperature, which is different from the conductivity behavior of PH1000 film prepared from the formulation added with EG where the conductivity is almost independent of the thermal annealing temperature or even without thermal annealing. The temperature dependence of the conductivity of PH1000 with PEG-TmDD could be ascribed to the decomposition of PEG-TmDD into EG and TmDD during thermal annealing. Because of the high conductivity and good wetting property with the addition of PEG-TmDD, the formulation of PH1000 with PEG-TmDD is used to fabricate the top electrode for inverted organic solar cells with vacuum-free processing. The cells exhibit an average fill factor of 60% and power conversion efficiency of 4.1% with P3HT:ICBA as the active layer.

2. Experimental section

2.1. Materials preparation and characterization

Surfactant PEG-TmDD (TOYNOL® Superwet-340, $M_w = 420$) was purchased from Tianjin SurfyChem T&D Co., Ltd. Different weight ratios of PEG-TmDD (0.4 wt%, 1 wt%, 4 wt%, 10 wt%) were added into the PEDOT:PSS (Clevios PH1000, Heraeus) to tune the contact angle and the conductivity of films. For comparison, 5 wt% ethylene glycol (anhydrous, 99.8%, Sigma-Aldrich) was added into PH1000 with 4 wt% PEG-TmDD as a reference formulation. To study the thermal

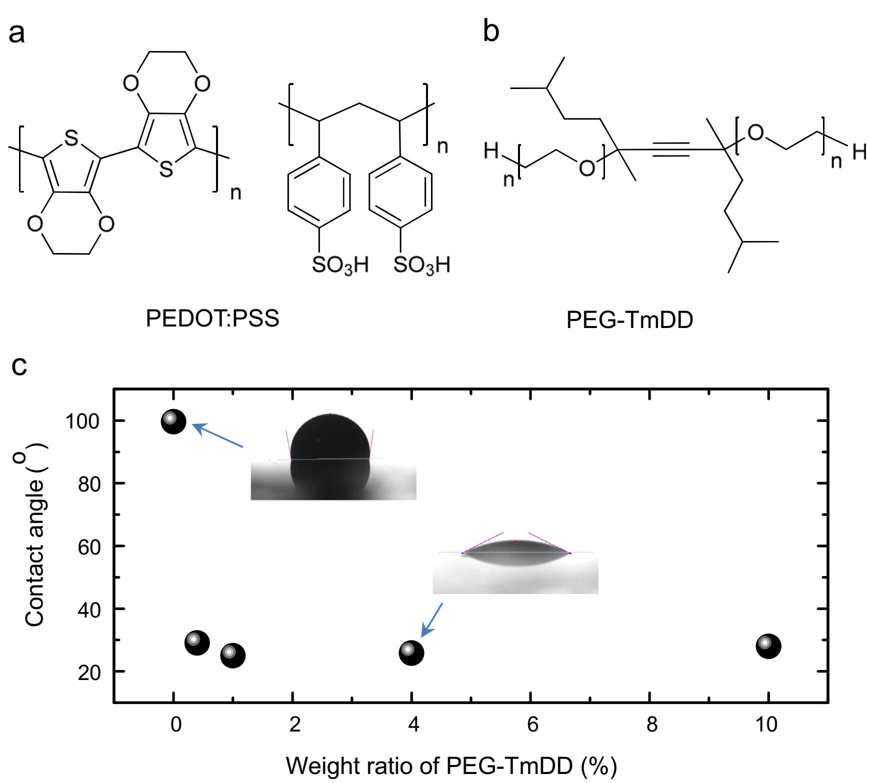

Fig. 1. Chemical structure of (a) PEDOT:PSS and (b) the nonionic surfactant PEG-TmDD; (c) contact angle of PH1000 aqueous solution with different weight ratios of PEG-TmDD (0 wt%, 0.4 wt%, 1 wt%, 4 wt%, and 10 wt%) on top of thermally annealed P3HT:ICBA films. The inset shows the contact angle of PH1000 solution and PH1000 solution mixed with 4% PEG-TmDD.