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Efficient ITO-free organic light-emitting diodes comprising PEDOT:PSS transparent electrodes optimized with 2-ethoxyethanol and post treatment

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We demonstrate highly conductive poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) films introduced with a newly investigated solvent 2-ethoxyethanol. The films are optimized by simple solvent post treatment and show enhanced conductivities and reduced sheet resistances. Solvent post treatment for 2-ethoxyethanol added PEDOT:PSS films reduces insulating PSS and forms conductive PEDOT networks in conductive films, resulting in improved electrical properties. ITO-free white OLEDs are fabricated with post-treated PEDOT:PSS electrodes and show almost equal performance to ITO-based OLEDs. Our work demonstrate that the conductive PEDOT:PSS electrode optimized by 2-ethoxyethanol and post treatment promises its potential as alternative transparent electrode in flexible, low-cost, high-performance ITO-free OLEDs.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted a great deal of attention as next-generation lighting sources and displays based on recent advances on the efficiency and stability of devices [1,2]. For low-cost and flexible OLEDs, the development of highly conductive transparent electrodes is of great necessity. The most commonly used material as a transparent electrode for organic optoelectronic devices is indium tin oxide (ITO) due to its many beneficial properties including high electrical conductivity and high optical transmittance [3]. However, ITO suffers from the intrinsic brittleness, the high material costs, and the need for the high processing temperature above 300 °C. These factors significantly limit ITO applications in low-cost devices on flexible substrates. For this reason, the need to develop alternative transparent electrodes as a replacement of ITO has been rapidly grown. Many emerging alternative transparent electrodes such as conductive polymers [4,5], silver nanowires [6,7], carbon nanotubes [8,9], graphenes [10,11], and metal grids [12,13] are investigated in recent years. Especially, conductive polymer poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) is one of the promising materials for alternative transparent electrodes owing to is high transmittance, conductivity, outstanding mechanical flexibility, and easy aqueous solution processing.

The pristine PEDOT:PSS formulations typically exhibit a low conductivity below 1–2 S/cm. For enhancing the conductivity of PEDOT:PSS thin films, high-boiling point solvents such as ethylene glycol (EG) and dimethyl sulfoxide (DMSO) are widely introduced [14–16]. These solvents readily increase the conductivity of films by more than two orders of magnitude. In addition, various organic solvents such as salts, acids, alcohols, ionic liquid or anionic surfactants are investigated for raising the conductivity of PEDOT:PSS thin films [17–19]. It is investigated that high-boiling solvents with high polarity such as DMSO and EG enhance the conductivity of

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PEDOT:PSS films caused by a strong screening effect between counter ions and charge carriers, which causes a reduction of Coulombic interaction between positively charged PEDOT and negatively charged PSS, resulting in morphological changes [20,21]. Treatment of PEDOT:PSS films with carboxylic, sulfuric acids or cosolvents can also remarkably improves the conductivity by inducing morphological changes of films and removal of insulating PSS [22–28]. Especially, strong-acid-based treatments using H_2SO_4 remarkably improve the conductivity of PEDOT:PSS films [24,29]. However, strong-acids may pose a potential health risk and safety issues. Thus, strong-acid-free treatment is more preferable to obtain highly conductive PEDOT:PSS films. We have reported that OLEDs and OPV cells employing conductivity enhanced PEDOT:PSS electrodes by various solvent treatment could yield comparable device performance to ITO reference electrode-based devices [15,25,30–32].

Here, we introduce highly conductive PEDOT:PSS films introduced with 2-ethoxyethanol and show high performance ITO-free OLEDs using the conductive polymer electrodes. The new solvent 2-ethoxyethanol greatly improves the conductivity of PEDOT:PSS thin films up to 761.7 S/cm. Moreover, the sheet resistance of the PEDOT:PSS films with 2-ethoxyethanol is remarkably reduced from 162.3 Ω/sq to 116.2 Ω/sq by simple methanol-based post treatment. The conductivity of post-treated PEDOT:PSS films with 2-ethoxyethanol reaches up to 940.9 S/cm. In addition, 2-ethoxyethanol results in better wettability on glass substrate in comparison with the conventional solvents such as EG and DMSO. ITO-free white OLEDs are fabricated with post-treated 2-ethoxyethanol added PEDOT:PSS electrodes and reveal comparable device performance to the reference ITO-based OLEDs. We believe that post-treated PEDOT:PSS electrodes added with 2-ethoxyethanol are promising alternative transparent electrodes for flexible, low-cost, high-performance ITO-free OLEDs.

2. Experimental section

2.1. Fabrication and characterization of PEDOT:PSS electrodes

PEDOT:PSS solutions (Clevios PH1000) were supplied by Heraeus, Germany. EG or 2-ethoxyethanol were mixed with PEDOT:PSS solutions and the formulations were spin-coated on glass substrates, pre-treated with UV/ozone for 10 min, at various speeds for 30 s. Subsequently, the films were baked on a hot plate at 120 °C for 15 min to dry films. For solvent drop post treatment, methanol was dropped on the PEDOT:PSS films. Subsequently, the post-treated films were heated at 120 °C for 15 min. Some of the PEDOT:PSS films were doped with fluorosurfactant Zonyl-FS300 (0.02–0.6 vol %) for better wettability.

Sheet resistance of films was examined by a van der Pauw method with a source measurement unit (Keithley 2401). Transmittance was measured by a UV–vis spectrophotometer. The transmittance values of thin films include the glass substrate. Thickness of films was examined by a surface profilometer (Alphastep 500, Tencor). The atomic force microscopy (AFM) images were obtained in tapping mode (Icon-PT, Bruker).

2.2. Fabrication and characterization of the OLEDs

White OLEDs were fabricated by thermal evaporation in a high vacuum chamber with a base pressure of around 10^{-8} mbar. ITO or various kinds of PEDOT:PSS electrodes investigated here were used as bottom electrodes for the devices. The PEDOT:PSS electrodes were carefully patterned by razor blade. The device structure was as follows (bottom to top): ITO or PEDOT:PSS films as a bottom electrode/10 nm 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HAT-CN)/50 nm N,N′-di (naphthalene-1-yl)N,N′-diphenyl-benzidine (NPB)/10 nm HAT-CN/50 nm NPB/10 nm HAT-CN/40 nm NPB/(total HTL thickness: 170 nm)/10 nm 4,4′,4″-tris(N-carbazolyl)-triphenylamine (TCTA)/5 nm 4,4′,4″-tris(N-carbazolyl)-triphenylamine (TCTA): Iridium (III)bis (4,6-difluorophenyl)-pyridinato-N,C2′)picolinate (FIrpic) (7 wt%)/0.5 nm TCTA: iridium (III)Bis(2-methyldibenzo [f,h]quinoxaline) (acetylacetonate) (Ir $(MDQ)_2$ (acac)) (5 wt%)/0.5 nm TCTA: tris (2-phenylpyridine)iridium (Ir $(ppy)_3$) (7 wt%)/5 nm 2,6-bis(3-(carbazol-9-yl)phenyl) pyridine (26DCzPPy): FIrpic (10 wt%)/50 nm 1,3-bis(3,5-dipyrid-3-yl-phenyl)benzene (BmPyPB)/1 nm LiF/100 nm Al. The active area of devices was 2 × 2 mm^2. All fabricated devices were immediately encapsulated with cover glass after thermal evaporation. The current-voltage-luminance characteristics and electroluminescence spectra were examined with a source-measure unit system (Keithley 238) and a goniometer-equipped spectroradiometer (Minolta CS-2000) [33].

3. Results and discussion

Chemical structures of PEDOT:PSS and 2-ethoxyethanol are shown in Fig. 1. 2-ethoxyethanol has a high-boiling point of about 135 °C. The conventional solvents with high-boiling point solvents and high polarity such as DMSO and EG effectively increase the conductivity of PEDOT:PSS films resulting from a strong screening

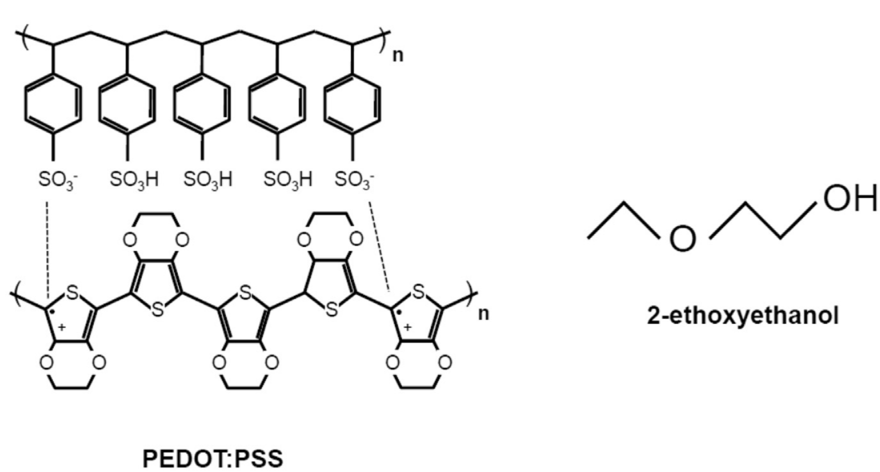

Fig. 1. Chemical Structures of a) PEDOT:PSS and b) 2-ethoxyethanol.