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Enhancement of conductivity and transparency for of poly(3,4-ethylenedioxythiophene) films using photo-acid generator as dopant

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ABSTRACT

We introduced the photoacid generator as dopant of photon energy to improve the conductivity of PEDOT:PSS films and form patterned film. The PEDOT:PSS film using PAG-001 exhibited the lowest sheet resistance of 156 Ω/sq at the photon energy of 1 J (10 wt% of PAG-001 in IPA). Also, the PEDOT:PSS film using PAG-301s exhibited the lowest sheet resistance of 154 Ω/sq at the photon energy of 1 J (10 wt% of PAG-301s in IPA). In terms of durability, the sheet resistance of the PEDOT:PSS film with PAG increased to 10% after 10 days, which shows better stability than that of PEDOT:PSS film with DMSO (10% 3 days). We introduced piperidine to increase sheet resistance gaps between conductive and insulating region. In the case of piperidine treatment, the sheet resistance of the conductive region showed 243 Ω/sq, and that of the insulating region showed $2.6^{*}10^{7}$ Ω/sq. In one film, the difference of sheet resistance between the conductive and insulating regions increased from 10^3 to 10^5 times.

1. Introduction

Nowadays, optoelectronic devices, such as liquid crystal displays, light-emitting diodes, solar cells, touch panel displays, lasers, and detectors, are attracting immense attention owing to their wide application in many areas [1,2]. For optoelectronic devices, at least one electrode is required to be transparent in order to emit or harvest light. Thus, the most popular material used as a transparent electrode is indium tin oxide (ITO). ITO has high transmittance and conductivity, and thus exhibits excellent performance as a material for optoelectronic devices. However, as indium is a rare earth metal, it is very expensive owing to its scarcity. Moreover, as ITO is not flexible, it is not suitable for use in next-generation flexible electronic devices, which require materials with transparency, flexibility, and conductivity [3–8].

Many materials, including conducting polymers [9–13], silver nanowires [14], carbon nanotubes [15,16], and graphenes [17,18], have been investigated as transparent electrodes for optoelectronic devices. Among them, poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is the most successful conducting polymer for commercial applications. It can be dispersed in water and some organic solvents, and high-quality PEDOT:PSS films can be readily coated on substrates using conventional solution processing techniques, such as coating and printing. In addition, PEDOT:PSS films have high transparency in the visible range, high mechanical flexibility, and excellent thermal stability [19–25]. Nonetheless, PEDOT:PSS exhibits low conduction characteristics because the (−) charged PSS-rich surface layer surrounds the (+) charged short PEDOT chain in water-dispersed PEDOT:PSS [26–29].

Several methods have been reported to significantly enhance the conductivity of PEDOT:PSS, including the addition of an organic compound, such as ethylene glycol and dimethyl sulfoxide (DMSO), ionic liquid, anionic surfactant, or dimethyl sulfate into PEDOT:PSS [29–34]. When Lee et al. introduced H2SO4 into PEDOT:PSS (Clevios PH1000), the conductivity of PEDOT:PSS was improved by 4380 S/cm^2. The addition of H_2SO_4 as a secondary dopant improved the morphology of PEDOT:PSS, leading to an increase in the conductivity of the PEDOT:PSS film [35,36].

An optoelectronic device with ITO is obtained by adjusting the electrons of the conductive and insulating parts. However, in the case of a patterned substrate, a hologram pattern is generated,

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which can be easily observed by the human eye owing to the interval of the pattern. Owing to this problem, the optical characteristics are affected by the scattering light and deviation of transmittance owing to the pattern formed by the device. Many studies have reported the patterning of PEDOT:PSS with enhanced conductivity for use as an optoelectronic device [37–41].

We investigated the formulation of PEDOT:PSS with a photoacid generator (PAG) of various structures. PAG releases strong organic acids at a specific absorption wavelength. These organic acids induce phase separation between PEDOT and PSS and improve the conductivity [42]. In addition, an organic acid containing a fluoro group is introduced into the PEDOT:PSS film to achieve hydrophobicity on the surface. Consequently, moisture is blocked in the device, and hence, the sheet resistance does not change and the durability is improved [43–49].

When using a patterned substrate, the difference between the sheet resistance of the conductive and insulating parts must be more than ~10^5 times. Pristine PEDOT:PSS exhibits a sheet resistance of ~10^5 Ω/sq, and the PEDOT:PSS with a PAG exhibits a sheet resistance of ~10^2 Ω/sq. Therefore, the sheet resistance difference is only 10^3 times. We used piperidine in PEDOT:PSS to create a more complete insulation pattern. Consequently, the sheet resistance was increased to ~10^7 Ω/sq and the sheet resistance of the part with PAG was improved to 224 Ω/sq. Finally, we fabricated non-visible and selectively patternable films [44].

2. Experimental section

2.1. Materials

PEDOT:PSS with PH1000 (1.0–1.3 wt% in H2O, viscosity = 15–50 mPas, pH = 1.5–2.5) was purchased from Clevios™. 2-Naphthyl-diphenylsulfonium Trifluoro-methanesulfonic acid (PAG-001) and Butyl-(4-butylsulfanyl-1-naphthyl)-1-naphthyl sulfonium Trifluoro-methanesulfonic acid (PAG-301s) (PAG) (Loum High Tech) and cis-2,6-dimethylpiperidine (piperidine) (≥97.0% (GC), Sigma–Aldrich) were used as additives. Scheme 1 shows the chemical structure of the additives.

2.2. Preparation of PEDOT film

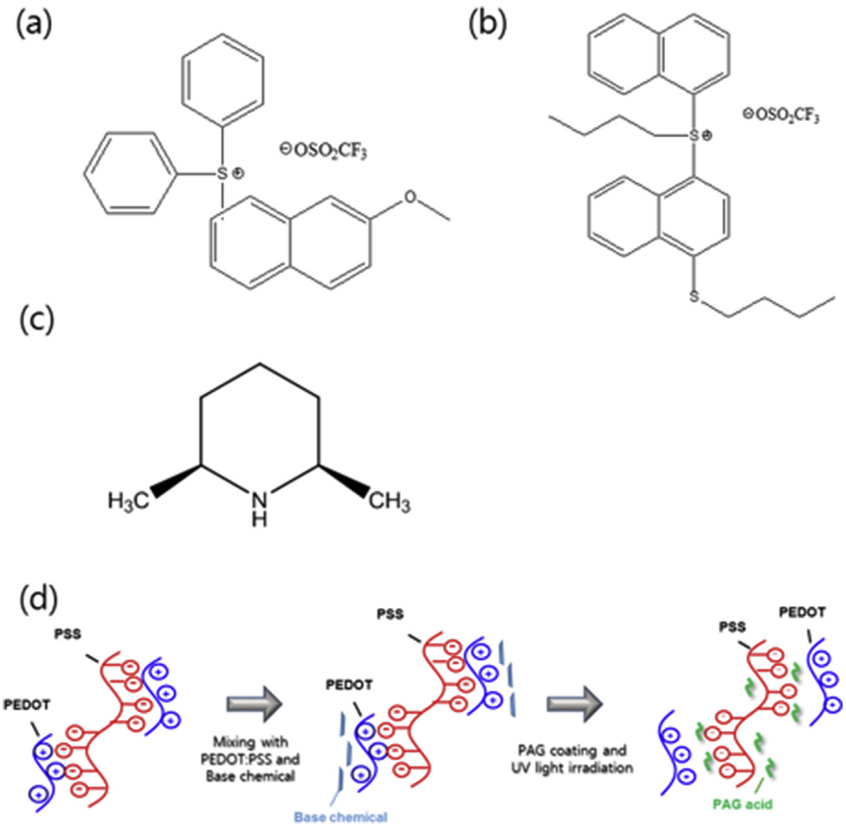
Glass substrates were washed with acetone, isopropyl alcohol (IPA), and distilled water using an ultrasonic bath, followed by nitrogen blowing and subsequent drying in a vacuum oven.

Two types of conductive films were prepared: a film in which PAGs (PAG-001, PAG-301s) were added to the PEDOT:PSS film and a film in which PAG and piperidine were added to the PEDOT:PSS film.

For the preparation of the first film, PAG was diluted to a concentration of 5–20 wt% in IPA. The diluted PAG was thereafter deposited on a substrate coated with PEDOT:PSS film.

For the preparation of the second film, a piperidine–PEDOT:PSS solution was prepared by adding 1 wt% or 5 wt% piperidine to PEDOT:PSS solution. The piperidine–PEDOT:PSS solution was coated on a substrate. Subsequently, a solution of PAG diluted to 10 wt% in IPA was coated on the piperidine–PEDOT:PSS film.

The PEDOT:PSS film was manufactured using a layer-by-layer method in which PAG solution was coated on a substrate of PEDOT:PSS or piperidine–PEDOT:PSS via spin coating. The piperidine–PEDOT:PSS solution was filtered using a 0.45 μm syringe filter and used as the coating solution. The solution was coated via spin coating at 2000 rpm for 30 s. In all the cases, the solution was



Scheme. 1. Chemical structure of various additives used in this study: (a) PAG-001, (b) PAG-301s, (c) cis-2,6-dimethylpiperidine, (d) Schematic illustration of the mechanism of conductivity enhancement of PEDOT:PSS with PAG.