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Random mesh-like Ag networks prepared via self-assembled Ag nanoparticles for ITO-free flexible organic solar cells

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ABSTRACT

Highly-transparent and flexible random mesh-like Ag networks formed by self-assembled Ag nanoparticles for use in transparent and flexible electrodes for ITO-free flexible organic solar cells (FOSCs) was demonstrated. By transferring a self-assembled Ag nanoparticle network onto a PET substrate, embossed and intaglio-type mesh-like Ag network electrodes were fabricated. Electrical, optical, morphological, and mechanical properties of the embossed and intaglio-type mesh-like Ag network electrodes were compared in detail. Although both mesh-like Ag networks exhibited similar sheet resistance, optical transmittance, and flexibility, the intaglio-type Ag networks were advantageous to use as transparent electrodes for FOSCs due to the high aspect ratio of emboss-type Ag networks. Regardless of organic active materials, FOSCs with intaglio-type Ag networks exhibited better performance than FOSCs with emboss-type Ag networks due to ease in forming uniform organic layer coatings on the intaglio-type Ag networks embedded in the substrate. This indicated that intaglio-type mesh-like Ag network electrodes are a promising flexible and transparent anode for printable ITO-free FOSCs.

1. Introduction

Due to several advantages possessed by flexible organic solar cells (FOSCs), such as their; low-cost, large-scale fabrication capability, compatibility with flexible substrates, and simple printing-based processing, the FOSCs have been considered as next generation photovoltaics to replace conventional Si-based photovoltaics [1,2]. In particular, printing-based continuous and atmospheric coating processes are of significance merit to FOSCs toward realizing low-cost and disposable energy harvesting devices. Recently, extensive research has been performed with regard to organic materials and FOSCs printing processes in both academia and industry, which has rapidly increased the performance of FOSCs, creating the expectation of mass-produced and cost-efficient FOSCs in the near future [3–7]. Among the several layers making up FOSCs, flexible transparent electrodes (FTEs) are a key component affecting the performance, flexibility, reliability, and cost of FOSCs [8–10]. However, most FOSCs modules have been fabricated on sputtered Sn-doped In_2O_3 (ITO) films in both academia and industry research, due to their low sheet resistance, high transmittance, and large area coating via roll-to-roll (RTR) sputtering, despite the high costs of ITO/PET substrates [11–14]. To reduce fabrication costs and enhance the competiveness of FOSCs versus conventional Si photovoltaics, high-cost ITO electrode should be replaced with cost-effective and printable FTEs. Recently, printable FTEs, such as Ag nanowires, conducting polymers, carbon nanotubes and Ag grids for ITO-free FOSCs have been reported as replacement to high-cost ITO films [15–21]. Among several printable FTEs, printable metal-grids or metal networks have considerable attention as replacements to high-cost ITO electrodes. As discussed by Liu et al., high-resolution Ag grid electrodes embedded in PET substrates facilitated charge transport and collection from the conductive PEDOT:PSS (PH1000) layer during FOSC operation [22]. Yu et al., also reported that ITO-free FOSCs with screen-printable Ag grids (honeycombs or lines) embedded in barriers showed power conversion efficiencies of 1.82% and 1.92% [23]. M. Hösel et al. reviewed the characteristics of several printable electrode materials for RTR processed FOSCs and suggested a possibility of ITO-free printable FOSCs [24]. Recently, Bing et al., suggested self-forming metallic network electrodes fabricated via cracked gel films demonstrating low sheet resistance values of 4.2 Ω/square and high optical transmittance values of 82% [25]. Kiruthika and coworkers also reported cracked template-based transparent Cu network electrode with sheet

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resistance of 5 Ω/square and transmittance of ~75% [26]. They reported the rod-coated colloidal layer serve as a template for selective deposition of Cu in the crack region. Based on cracked polymer templated Ag network, they demonstrated ITO-free FOSCs with power conversion efficiency of 2.14%, which is comparable to ITO-based reference FOSCs (2.27%) [27]. Furthermore, they suggested spray-roll coating process for cracked template-based metal network electrodes for large-area metal network FTEs [28]. However, they still employed complicated cracked template fabrication and etching process, which are not idea for cost-efficient printable FOSCs. Therefore, the development of printable template-free mesh-like metal network electrodes is imperative toward realizing all-printable ITO-free FOSCs.

In this study, we report ITO-free FOSCs fabricated onto transparent and flexible random mesh-like Ag networks formed via template-free self-assembled Ag nanoparticles. The electrical, optical, morphological, and mechanical properties of emboss- and intaglio-type Ag network electrodes, which were thermally transferred onto PET substrate, were compared in detail. Additionally, the performance of FOSCs fabricated onto emboss- and intaglio-type Ag network electrodes was compared to determine the proper type of self-assembled Ag network for ITO-free FOSCs. Based on the performance of the ITO-free FOSCs, we evaluated the suitability of intaglio-type Ag networks embedded in PET substrate as promising FTEs to replace high-cost ITO films.

2. Experimental

Template-free random-mesh like Ag network electrodes were fabricated via bar-coating and thermal transfer techniques onto polyethylene terephthalate (PET) substrates (SANTE®, Cima Nanotech Inc.) [29]. A dilute-alloyed Ag nanoparticle ink consisted of 0.2 g resin (BYK-410) and 4 g Ag nanoparticles in a mixed solvent of 30 g 1,2-dichloroethane($C_2H_4Cl_2$) and 15 g deionized water. The Ag nanoparticle ink was sonicated at 180 W for 2 min to homogenize the Ag ink. Then, the Ag nanoparticle ink was coated on the PET substrate using a conventional Meyer rod coating system. Prior to Ag nanoparticle ink coating, the surface of the PET substrate was pre-treated by 3-aminopropyltriethoxysilane ($C_9H_{23}NO_3Si$) with 1% acetone solution. The pre-treated PET substrate was stuck on a flat plate and a Meyer rod is subsequently pulled over the Ag nanoparticle ink and PET substrate at a scan speed of 30 mm/sec. The wet coating of Ag nanoparticle on PET substrate is carefully dried to remove the solvent at 50 °C for 30 min in a formic acid gas-filled box to make self-assembled emboss-type Ag network. As illustrated in Fig. 1, dilute-alloyed Ag nanoparticles were coated onto the PET substrate via a simple Meyer rod coating. Substrate heating led to solvent evaporation and the formation of a random mesh-like Ag network. Because the mesh-like Ag network formed via the self-assembly of Ag nanoparticles onto the PET substrate, this sample was referred to as an emboss-type Ag network because the Ag network protruded from the PET substrate. In the case of the intaglio-type Ag network, fabrication was performed via thermal transfer processes from a mother PET to a target PET substrate as shown in Fig. 1. To transfer the mesh-like Ag network, an adhesive resin and target PET were coated directly onto the emboss-type Ag network structure, respectively. Thermal heating of the sample subsequently led to transfer of Ag network from mother PET to target PET substrate. Because the mesh-like Ag network fabricated by the transfer method was embedded within the PET substrate, the sample was referred to as an intaglio-type Ag network. The pictures in Fig. 1 show the high optical transparency of the emboss- and intaglio-type mesh-like Ag networks fabricated onto PET substrates. The sheet resistance and optical transmittance of the mesh-like Ag network films was measured using a four-point probe (FPP-HS8, DASOL ENG) and UV-Visible spectroscopy (V-670, Jasco) between a wavelength range of 200–1200 nm. The surface morphologies of the emboss- and intaglio-type Ag network films were examined via a field emission scanning electron microscope (FESEM, LEO SUPRA 55) with an operating voltage of 10 keV and via atomic force microscopy (AFM, PUCO Station STD). Mechanical properties of the mesh-like Ag network films were evaluated via a specially designed inner and outer bending test system. The outer bending test induced tensile stress onto the Ag network film, while the inner bending test induced compressive stress. Dynamic fatigue bending tests were carried out using a lab-designed cyclic bending test machine at a frequency of 0.5 Hz for 10,000 cycles. During the repeated bending test, the resistance of the mesh-like Ag network was measured as a function of bending cycle. Additionally, a twist bending test of the mesh-like Ag network was performed.

To evaluate the feasibility of mesh-like Ag network films as FTEs for ITO-free FOSCs and determine proper type of Ag network electrode, conventional bulk heterojunction FOSCs were fabricated. As a reference sample, DC sputtered ITO/PET samples with a sheet resistance of 55.3 Ω/square and an optical transmittance of 85.1%

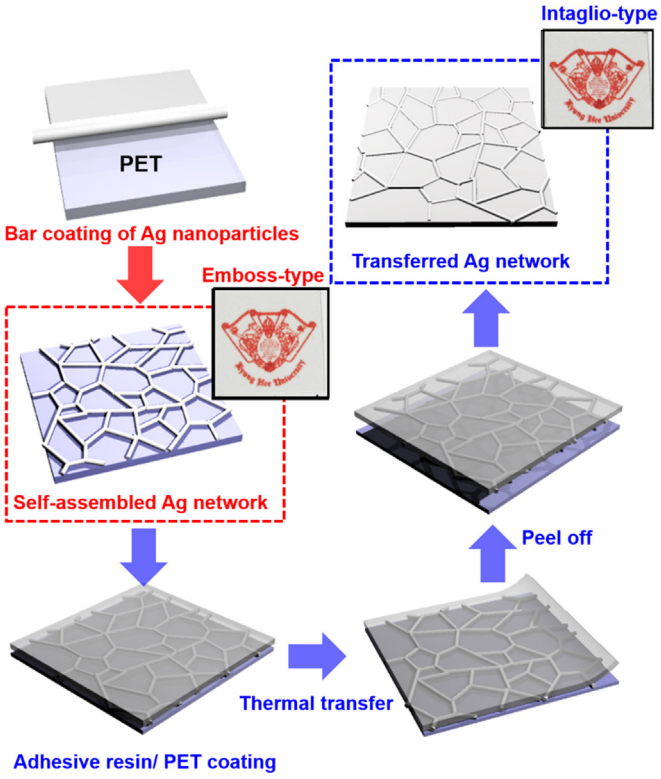

Fig. 1. Schematics for the coating of self-assembled Ag nanoparticles and the thermal transfer process to fabricate emboss- and intaglio-type mesh-like Ag networks onto PET substrates (SANTE®, Cima Nanotech Inc.). The picture reveals the optical transparency of mesh-like Ag networks coated onto PET substrates (Emboss-type) and embedded within the PET substrates (Intaglio-type).

Table 1
Sheet resistances of the emboss- and intaglio-type Ag network electrodes and reference ITO films.

	Emboss-Ag/PET	Intaglio-Ag/PET	ITO/PET
Sheet resistance [Ohm/sq.]	12.50	3.95	55.3
Transmittance at 550 nm [%]	86.5	83.1	85.6
Average transmittance (400–800 nm [%])	84.4	82.3	85.1