Journal of Industrial and Engineering Chemistry xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Short communication

Micromesh carbon nanosheet electrodes fabricated by phase-separation of immiscible polymer blends

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ARTICLE INFO

Article history:
Received 31 October 2017
Received in revised form 10 January 2018
Accepted 31 January 2018
Available online xxx

Keywords:
Phase-separation
Micromesh structure
Carbon nanosheets
Transparent conductive electrodes
Organic photovoltaics

ABSTRACT

We adopt micromesh structure in carbon nanosheets (M-CNS) fabricated by phase-separation of immiscible polyacrylonitrile/poly(methyl methacrylate) blend precursors to improve their properties as a transparent conductive electrode. The facile approach without any time-consuming patterning processes can improve trade-off between sheet resistance and optical transmittance of conventional CNS. The M-CNS exhibits improved sheet resistance of ~50% without compromising optical transmittance, leading to a high power conversion efficiency of ~2.07% for M-CNS electrode-based organic photovoltaics.

Introduction

Transparent conductive electrode (TCE) is an indispensable component in optoelectronic devices such as organic/perovskite photovoltaics and light-emitting diodes, in which at least one side should be transparent [1,2]. Conventional TCEs have been based on metal oxides, represented by indium tin oxide (ITO), because of their low sheet resistance (10–30 $\Omega\,sq^{-1}$) and high optical transmittance (>90%) [3,4]. However, these TCEs based on metal oxides appear to be increasingly problematic in the great advancement of optoelectronic devices, which requires all layers and materials in the devices to be cost-effective, lightweight, and highly flexible [5–7]. In this point of view, concerns on conventional TCEs have been raised over their vacuum-based manufacturing, scarcity of indium, and brittleness [4–10]. Thus, the development of next-generation TCE is a critical step not only in TCE itself but also in potential application fields such as optoelectronic devices.

Among various materials, graphene derivatives have gained prominence as a viable alternative due to their high mechanical strain (>15%), high transmittance (>90%), and low sheet resistance (<200 $\Omega\,sq^{-1}$) [11–13]. Chemical vapor deposition (CVD) has been regarded as the most effective technique to produce highly transparent and conductive graphene films [13–16]. Also, the feasibility of graphene as a TCE has been generally demonstrated by CVD graphene. Despite the promising properties of CVD graphene as a transparent conductor, additional and complex processes of removing metal catalysts and transferring CVD graphene onto a target substrate are inevitable, resulting in a significant increase of manufacturing costs [13–16]. Meanwhile, more facile and cost-effective routes to produce graphene have been reported. For example, the use of chemical exfoliation for reduced graphene oxides (rGO) guarantees mass production and solution-processing of graphene [17–21]. However, a large number of structural defects make the electrical characteristics of rGO much worse than those of the conventional graphene, leading to significantly poor performances of the devices employing rGO-TCEs [17,18].

As another promising strategy, we previously developed highly conducting carbon nanosheets (CNSs) via simple solution-processing; the CNSs were converted from polymeric carbon precursors such as polyacrylonitrile (PAN), which are soluble in polar organic solvents [22–26]. The potentials of the CNS-TCEs through their direct evaluation in organic photovoltaics (OPVs) have been verified in terms of both performance and flexible applications [23–26]. However, due to still higher sheet resistance (~3 $k\Omega\,sq^{-1}$) and lower optical transmittance (~60%) compared to those of the

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https://doi.org/10.1016/j.jiec.2018.01.039
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Please cite this article in press as: S.-Y. Son, et al., Micromesh carbon nanosheet electrodes fabricated by phase-separation of immiscible polymer blends, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.01.039

ITO-counterpart, the widespread application of the CNS-TCEs in optoelectronic devices has been limited.

In this work, for the first time, we newly developed CNS with micromesh structure (M-CNS) to improve TCE characteristics of the CNS via phase-separation of polymeric precursors. One-step micromesh patterning involves only spin-coating of immiscible PAN/poly(methyl methacrylate) (PAN/PMMA) blend, followed by conventional processes for CNS fabrications. Furthermore, the resulting M-CNS and its characteristics could be simply modulated by coating conditions such as concentrations of blended solutions, and ratios between PAN and PMMA. This approach can improve conventional trade-off between sheet resistance and optical transmittance of pristine CNSs without compromising processing advantages. As a result, OPV employing the M-CNS provided better performance than traditional CNS-based devices, showing an increase of about 18% in power conversion efficiency (PCE).

Experimental

Synthesis of M-CNSs

M-CNSs were synthesized using PAN/PMMA blends as a precursor. Weight average molecular weights of PAN (Sigma–Aldrich) and PMMA (Sigma–Aldrich) are 150,000 and 120,000 g mol^{-1}, respectively. PAN/PMMA blends ranged from 2 to 7 wt% were prepared in *N*,*N*-dimetylformamide (DMF, Fisher). Blend ratio of PAN/PMMA was fixed at a weight ratio of 4:6. PAN/PMMA blends were spin-coated onto clean quartz substrates with a size of $1.5 \times 1.5\ \text{cm}^2$. Then, the quartz substrates were washed in acetone and isopropyl alcohol for 30 min each. Spin-coated PAN/PMMA blend films were stabilized at 270 °C for 2 h in an air atmosphere, and then carbonized to 1200 °C at a ramping rate of 5 °C min^{-1} under a H_2 (10%)/Ar (90%) mixture.

Characteristic evaluation of M-CNSs

To analyze morphological properties of M-CNSs, surface morphologies and thickness of M-CNSs were confirmed by an optical microscope system (BX51, Olympus) and an atomic force microscopy (AFM, Dimension 3100, Veeco), respectively. Sheet resistance and transmittance of M-CNSs were measured by a four-point probe system (MCP-T610, Mitsubishi chemical analytech Co., Ltd.) and an UV/VIS/NIR spectrophotometer (V-570, Jasco), respectively.

Performance evaluation of M-CNS electrode-based OPVs

To fabricated M-CNS electrode-based OPVs, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Clevios) as a hole transfer layer was spin-coated onto M-CNSs and then dried at 150 °C for 10 min. A solution with 50 mg of poly(3-hexylthiophene) (P3HT, Rieke Metals) and 50 mg of [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM, Nano-C) in 2 mL of 1,2-dichlorobenzene was spin-coated onto the resulting surface in a N_2 glove box. Subsequently, the surface was annealed at 150 °C for 10 min. Finally, Ca (25 nm)/Al (80 nm) layers were thermally deposited at 10^{-6} Torr using a thermal evaporator system. To analyze the performance of the OPVs, current density (J)–voltage (V) curves of the cells were measured using a Keithley 1200 instrument under 100 mW cm^{-2} illumination with air mass (AM) 1.5 global (G) conditions.

Results and discussion

We utilized phase-separation phenomenon of an immiscible PAN/PMMA blend to fabricate M-CNS transparent conducting films, where PAN is a precursor for CNS and PMMA is a sacrificial material for porous structures. With an aid of the phase-separation, micromesh structures in CNS films could be obtained by facile solution-process without any time-consuming patterning processes such as template-based methods, synthesis of block co-polymers, ion beam, and chemical etching [27,28]. As shown in Fig. 1, M-CNS films were fabricated by three steps: spin-coating of PAN/PMMA blend, stabilization, and carbonization of the films. First, spin-coating of PAN/PMMA blend leads to phase-separation in polymer films. In general, immiscible polymer blends are known to have segregated domains, where each domain is predominantly composed of an individual homo-polymer [29]. Also, a shape and size of domains can be controlled by experimental conditions such as polymer molecular weight, solution concentration, and blend ratio [30,31]. Next, the spin-coated PAN/PMMA blend films with sea-island morphology are converted into M-CNS films through subsequent heat-treatments. It is well known that PAN can be converted into carbonaceous materials with carbon content of more than 90% after stabilization and carbonization processes [22]. In contrast, PMMA is decomposed and removed by heat-treatments due to its low thermal-stability [32]. These different behaviors in heat-treatments were confirmed by thermogravimetric analysis (TGA) as provided in Fig. S1. After the carbonization process, carbon yields of pure PAN and PMMA are 36 and 0%, respectively.

Blend ratios of PAN to PMMA were controlled to prepare ideal porous morphology of M-CNS films as TCEs. As shown in Fig. S2, a size of PMMA domains as the hole increased with an increase of PMMA content, and elongated domains appeared when weight ratio of PAN to PMMA was 2:8. Considering that percolated networks of PAN provide the conducting path and PMMA domains are eliminated in carbonization, which could improve transmittance, it is believed that the blend ratio of 4:6 is the most desirable for M-CNS films. After the optimization of blend ratios, we controlled concentration of the PAN/PMMA blend solutions from 2 to 7 wt%, as shown in Fig. 2. Even though all M-CNS films showed

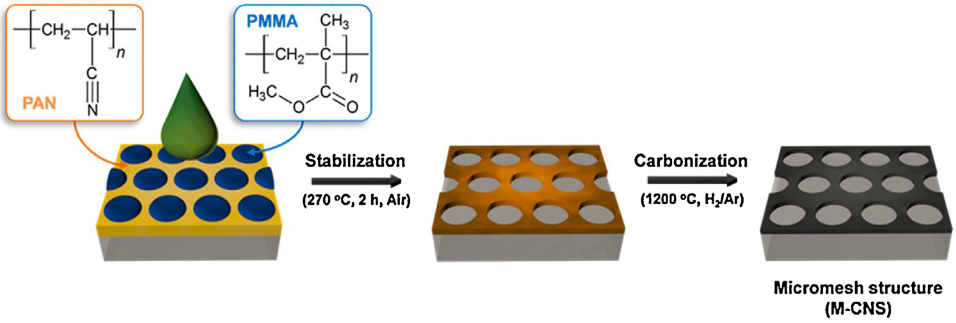

Fig. 1. A schematic illustration on fabrication of M-CNS films by phase-separation of immiscible PAN/PMMA blends.

Please cite this article in press as: S.-Y. Son, et al., Micromesh carbon nanosheet electrodes fabricated by phase-separation of immiscible polymer blends, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.01.039