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Core-shell structure and closest packing of electrically conductive polymer/carbon nanotube hybrid: High electrical conductivity of bucky paper

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ABSTRACT

The crucial obstacle to design an electrically conducting device is the poor and heterogeneous dispersion of the pristine CNTs in polymer matrices. The best method to overcome these problems is to create a CNT core-polymer shell structure, allowing a dense close-packing of the CNT core-polymer shell units, expecting in the formation of completely homogeneous CNT-polymer films and a big improvement in their physicochemical properties including the electrical conductivity. Poly[3-(5-carboxylpentyl)thiophene-2,5-diyl] wrapped multi-walled carbon nanotubes (P3PT-COOH/CNTs) in core-shell structure were successfully prepared as a bucky paper by simple pH-control of the aqueous solution containing different weight percentages of the both components (P3PT-COOH/CNTs = 50/50, 60/40, 70/30). The core-shell structure of P3PT-COOH/CNT-50 nanohybrid films showed a significantly high electrical conductivity increase of up to 17 fold compared with those of non-core-shell structure prepared by a simple mixing (e.g. from 1.33 to 1.81 S/cm up to 22 S/cm). The result could be considered to be a consequence of a homogeneous P3PT–COOH–wrapping on the surface of CNTs, the regular shell thickness of individual CNT-core/P3PT–COOH–shell nanohybrid fibers, and their three-dimensional close packing in a film.

1. Introduction

Multi-walled carbon nanotubes (CNTs) have attracted increasing attention due to their unique mechanical, electrical, thermal, and structural properties [1–5]. Carbon nanotubes have well ordered, long, hollow nanostructures consisting of carbon atoms bonded to each other through sp^2 hybridized bonds. The application of the excellent electrical properties of CNTs are also increasing in various fields where one wants to design electrically conductive devices, such as in thin-film transistors [6–8], field-emission displays [9,10], hydrogen fuel storage devices [11–13], and sensors [14–16]. Many attempts to prepare flexible and highly electrically-conducting organic polymers have been made by mixing of the pristine CNTs with organic solutions of polymers or directly in polymer melts, resulting in significant level of CNT-lump presence in the polymer matrices and formation of electrically poor conductive CNT-polymer nanocomposites [17–20].

The crucial obstacle to design an electrically conducting device is the poor and heterogeneous dispersion of the pristine CNTs in polymer matrices [21]. As a result, the pristine CNTs are aggregated and exist as a bundle in their native state. For these reasons, it is highly desirable to develop an efficient and simple method not only individually to dissolve CNTs in polymer matrices, but also to control concentration of CNTs, resulting in increment of the CNT-interconnectivity within the polymer matrix, which translates the individual CNT properties into the whole composite.

The best method to overcome these problems is to create a CNT core-polymer shell structure, allowing a dense close-packing of the CNT core-polymer shell units, expecting in the formation of completely homogeneous CNT-polymer films and a big improvement in their physicochemical properties including the electrical conductivity [22–24]. Moreover the choice of electrically conducting polymer as a non-covalently CNT-decorating organic

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material will provide an opportunity to generate flexible and highly electrically-conducting CNT-based nanohybrid films. Poly(3-alkylthiophene) as a family of conjugated polymers has shown relatively good electrical conductivity at around 10^{-6}–10^{-8} S/cm and has been reported to be a best candidate for electrically conductive devices [25,26]. For example, poly [3-(5-carboxylpentyl)thiophene-2,5-diyl] (= P3PT-COOH), which has the hydrophobic thiophene ring backbone and the hydrophilic carboxyl group, could also be a good candidate to be used for the non-covalent and core-shell structured decoration of individual CNT molecules with the significantly high electrical conductivity of about 61.7 S/cm [27,28].

The goal of this study is the development of an efficient method to produce homogeneous P3PT-COOH/CNT nanohybrides in core-shell structure with high electrical performance. The excellently high electrical properties of P3PT-COOH/CNT nanohybrid bucky papers with core-shell structure could be expected to be effectively applied in various fields for electrically conductive devices, such as in thin-film transistors, field-emission displays, and sensors.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (CNTs, >95%, 20–30 nm outer diameter, 10–30 μm length) were purchased from M-Power (Korea). Pristine multi-walled carbon nanotubes (CNTs) were refluxed in 5 N HCl solution to remove metallic components for one day prior to use. Poly [3-(5-carboxylpentyl)thiophene-2,5-diyl], P3PT-COOH, was prepared by the literature procedure [29]. Room temperature ionic liquid (RTIL) 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim]BF_4; mp = −71 °C) as liquid porogen was purchased from C-Tri Co., Ltd. (Korea). All supplementary chemicals including NH_4OH solution and organic solvents were purchased from Sigma–Aldrich (USA) at analytical grades and used without further purification.

2.2. Preparation of P3PT-COOH/CNT nanohybrides with a core-shell structure

A typical procedure for preparing P3PT-COOH/CNT nanohybrides with a core-shell structure is as follows: i) P3PT-COOH (600, 720, or 840 mg) were dissolved in 30 mL of 5% NH_4OH solution and then CNTs (600, 480, or 360 mg) were homogenized in the P3PT-COOH solution with assistance of a homogenizer (Sonosmasher, ULH-700S) (Ulsso Hightech, Cheongwon-gun, Korea); ii) The basic P3PT-COOH/CNT solutions (P3PT-COOH/CNT-50 (50/50), P3PT-COOH/CNT-40 (60/40), and P3PT-COOH/CNT-30 (70/30)) were slowly neutralized by adding 2 N HCl solution followed by dialysis (membrane tubing, molecular weight cutoff 12000–14000, Spectrum Laboratories, Savannah GA, USA) against distilled water for 3 days to remove possible small molecules; iii) After adding 1-buyl-3-methyl imidazolium tetrafluoroborate ([bmim]BF_4, mp = −71 °C) (1, 2, or 4 g), pouring into a mold, vaporizing the aqueous solvent, and removing [bmim]BF_4, the black-colored P3PT-COOH/CNT films (P3PT-COOH/CNT-50-1~4, P3PT-COOH/CNT-40-1~4, and P3PT-COOH/CNT-30-1~4) were obtained (see Table 1). The average yield amount was found to be 98%. Here, [bmim]BF_4 as a room temperature ionic liquid (RTIL) was used as a liquid porogen to obtain the P3PT-COOH/CNT nanohybrides as flat bucky paper.

2.3. Preparation of P3PT-COOH&CNT samples with non-core-shell structure

In principle, P3PT-COOH&CNT bucky papers with non-core-shell structure were prepared very similar method to the procedure for preparing P3PT-COOH/CNT nanohybride bucky papers. However, the method does not include the neutralization step as a CNT-core and P3PT–COOH–shell formation process. In detail, the procedure is as follows: i) P3PT-COOH (600, 720, or 840 mg) were dissolved in 30 mL of 5% NH_4OH solution and then CNTs (600, 480, or 360 mg) were homogenized in the P3PT-COOH solution with assistance of a homogenizer (Sonosmasher, ULH-700S) (Ulsso Hightech, Cheongwon-gun, Korea); ii) After adding [bmim]BF_4 (1, 2, or 4 g), pouring into a mold, vaporizing the aqueous solvent, and removing [bmim]BF_4 and all possible small molecules (or neutralization), the black-colored P3PT-COOH&CNT films (P3PT-COOH&CNT-50-1~4, P3PT-COOH&CNT-40-1~4, and P3PT-COOH&CNT-30-1~4) were obtained (see Table 1).

Table 1
a-c) core-shell structured P3PT-COOH/CNT nanohybrid film samples and d) no core-shell structured P3PT-COOH&CNT nanohybrid film samples. They were prepared by tuning of CNT concentration and RTIL amount.

	Sample name	CNT content (wt%)	RTIL content (g)
a)	P3PT-COOH/CNT-50-1	50	1
	P3PT-COOH/CNT-50-2	″	2
	P3PT-COOH/CNT-50-4	″	4
b)	P3PT-COOH/CNT-40-1	40	1
	P3PT-COOH/CNT-40-2	″	2
	P3PT-COOH/CNT-40-4	″	4
c)	P3PT-COOH/CNT-30-1	30	1
	P3PT-COOH/CNT-30-2	″	2
	P3PT-COOH/CNT-30-4	″	4
d)	P3PT-COOH&CNT-50-1	50	1
	P3PT-COOH&CNT-50-2	″	2
	P3PT-COOH&CNT-50-4	″	4

2.4. Characterization of P3PT-COOH/CNTs and P3PT-COOH&CNTs

3D morphologies of the samples were obtained using high-resolution transmission electron microscopy (HR-TEM; JEM 3010, JEOL, Japan) and scanning electron microscopy (SEM; JEOL and HITACHI S-3000H, Japan). P3PT–COOH–shell/CNT-core nanohybrid fiber unit and P3PT–COOH–shell thickness were observed using HR-TEM. The P3PT–COOH–shell/CNT-core nanohybrid fiber unit particles were dispersed in methanol, after which a drop of the solution was placed on a copper grid and allowed to air-dry. For SEM analysis, samples were sputter-coated with approximately 10 nm of gold before analysis. X-ray photoelectron spectroscopy (XPS; AES-XPS ESCA 2000, Thermo Fisher Scientific, United States) was applied for qualitative analysis of P3PT-COOH/CNTs with a core-shell structure and P3PT-COOH&CNTs with non-core-shell structure. Physicochemical properties of these prepared P3PT-COOH/CNT nanohybrides were examined by FT-IR spectrometer (JASCO 470 PLUS) and thermogravimetric analyzer (Seiko Exstar 6000 TG/DTA6100, Japan). Infrared spectra were recorded in solid condition at a range of 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) was conducted using 4 mg sample with a heating rate of 10 °C/min at temperatures ranging from 25 to 900 °C under air. Surface resistivity of samples initially were determined using a 4-point probe measuring instrument (FPP-400, BEGA, Korea) with 2 mm pin spacing and 700 μm pin radius and 10 mA current was used. This experiment was performed in triplicate using samples with the same horizontal and vertical length (2 × 2 cm) and different thicknesses. The volume electrical resistivity and the electrical conductivity were calculated from the surface resistivity as follows: Volume resistivity (ohm·cm) = surface resistivity (ohm/sq) × thickness (cm); Electrical conductivity (S/cm) = 1/volume resistivity (ohm·cm). X-ray photoelectron spectroscopy (XPS) was