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Systematic optimization of MWCNT-PEDOT:PSS composite electrodes for organic transistors and dye-sensitized solar cells: Effects of MWCNT diameter and purity

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) and polymer composites have attracted significant attention as metal-free electrode materials for various electronic devices. Many studies have presented strategies to enhance the electrical conductivity of MWCNT/polymer composites. However, systematic studies on the effects of MWCNT features on the composite properties are still missing. Such studies can further the development of MWCNT/polymer-based conducting materials. Herein, we characterize composite films of MWCNTs and poly (3,4-ethylenedioxythiophene) polymerized with poly(4-styrenesulfonate) (PEDOT:PSS), with variations in the MWCNT diameter and purity. MWCNT features greatly affect the physical/chemical/electrical properties of the MWCNT/PEDOT:PSS composite films. In addition, the diameter and purity of MWCNTs also influenced the transition behavior of the composite films during the hydrochloric acid-methanol treatment, which was performed for increasing electrical conductivity. As a result, we could optimize the performance of organic transistors and dye-sensitized solar cells (DSSCs) using MWCNT/PEDOT:PSS composite films as source/drain electrodes and catalytic counter electrodes, respectively. Furthermore, using the optimized device parameters, we successfully fabricated high performance fluorine doped tin oxide-free DSSCs and high-gain organic complementary inverters using MWCNT/PEDOT:PSS composite electrodes.

1. Introduction

Carbon-based conducting materials, such as carbon nanotubes (CNTs) and graphene, have received considerable attention as leading electrode materials in next-generation electronic devices due to their high conductivity, mechanical stability, flexibility, and optical transmittance [1–4]. Significant efforts have been devoted to enhancing the electrical properties of carbon-based nanomaterials; as a result, they have been successfully utilized as electrodes in a variety of electronic devices such as organic thin-film transistors (OTFTs), organic photovoltaic devices, dye-sensitized solar cells (DSSCs), and organic light-emitting diodes [2,4–9]. With rapid progress in CNT technology, their dispersion in common solvents, which has often been a problem, is now significantly improved. For example, polymer grafting and CNT oxidation have been found to increase the dispersion of CNTs in common solvents [10–14]. The combination of CNTs with a variety of polymers has also been studied and is considered an efficient route to developing highly soluble CNT-based composite materials [14–17].

In recent years, our group has reported several effective ways to enhance CNT dispersion in various polar solvents without degrading their inherent physical properties [18–22]. Wrapping CNTs with poly (3,4-ethylenedioxythiophene) polymerized with poly(4-styrenesulfonate) (PEDOT:PSS) resulted in the formation of completely dispersed multi-walled CNTs (MWCNTs) and PEDOT:PSS (MWPE) composite materials in water [18–22]. Furthermore, thin films of the MWCNT/polymer composites exhibited good electrical properties. By optimizing MWCNT concentration and performing various pre-/post-treatment processes, we could control the physical and electrical properties of the MWPE composite films. Ultraviolet (UV) oxidation, acid treatments, or doping with glycerol, and/or dimethyl sulfoxide led to considerable improvement in the surface properties, catalytic activity, optical transmittance, work function, and electrical conductivity

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of the MWPE films [19,21–23]. The resultant MWPE films successfully acted as high-performance electrodes in various electronic and optoelectronic devices. The electrical and surface properties of the films could be effectively adjusted to meet the requirements for each device depending on its functionality [19,21,22]. However, the effects of the physical properties of MWCNTs, including their diameter and purity, on the composite system are not yet fully understood despite their potential effect on the properties of MWPE composite films. Therefore, an in-depth study that systematically investigates the effects of MWCNT features on the MWPE composite film properties is necessary to better optimize the performance of MWPE-based electrodes for application in various electronic and optoelectronic devices.

In this study, we examined the physical/chemical/electrical properties of MWPE composite films according to the MWCNT diameter and purity. Four different types of MWPE composite films have been prepared and their surface morphologies, chemical structures, sheet resistances, work functions, and electronic band structures are compared. We also investigated the effects of hydrochloric acid-methanol (HCl-met) treatment on the surface and electrical characteristics of the different MWPE composite films. In addition, the device performances of OTFTs and DSSCs using the MWPE composite films as source/drain electrodes and catalytic counter electrodes, respectively, are compared. Finally, the optimized MWPE composite electrodes were used to replace fluorine doped tin oxide (FTO) in DSSCs while maintaining their high performance and to fabricate high-gain organic complementary inverters. Our work suggests that a proper choice of MWCNTs based on their diameter and purity is important to achieve optimal MWCNT-based composite electrode properties, depending on the device application.

2. Experimental section

2.1. Materials and sample preparation

PEDOT:PSS solution (CLEVIOS™ PH500, 1 wt.% in water) was purchased from H. C. Starck, while the MWCNTs were procured from Nano Solution. Table 1 summarizes the physical properties of the different types of MWCNTs used in this study. The MWCNTs were categorized into four different groups based on their diameter and purity – TMC 100-05, TMC 100-10, TMC 220-05, and TMC 220-10. TMC 220-05 and TMC 220-10 are the purified versions of TMC 100-05 and TMC 100-10, respectively, by chemical/mechanical refining processes. Both TMC 220-05 and TMC 220-10 exhibit much higher purities (90–95%) than the other samples (65–85%) due to the refining process. To prepare the MWPE solutions, 0.2 g of the MWCNTs was added to diluted PEDOT:PSS solutions (PEDOT:PSS 10 mL + deionized water 10 mL) without further purification. Consequently, four different MWPE films were prepared according to the diameter and purity of the MWCNTs. In addition, highly concentrated MWPE solutions were produced using TMC 220-10, which has outstanding electrical properties as well as high dispersibility (0.2 g, 0.3 g, and 0.4 g of TMC 220-10 in 20 mL of PEDOT:PSS). HCl-met treatment was carried out using typical solvent dipping and drying processes, as described previously [19,20]; the MWPE films were soaked in a solution consisting of 0.15 M HCl in a water/methanol (3:7 wt ratio) mixture for 5 min, followed by rinsing with deionized water and N_2 blowing.

Table 1
The physical properties of the MWCNTs used in this study.

MWCNT material	Diameter (nm)	Length (μm)	Purity (%)	Refining process
TMC 100-05	4–6	5–20	> 65	–
TMC 100-10	8–15	5–20	> 85	–
TMC 220-05	4–6	5–20	> 90	Chemical/ mechanical
TMC 220-10	8–15	5–20	> 95	Chemical/ mechanical

2.2. Characterization

The morphologies of the MWPE films were observed using an atomic force microscope (AFM, Veeco Nanoscope V). Sheet resistances of the MWPE films were measured using the 4-point probe method with a Keithley 2400 source meter. The chemical/electronic structures of the MWPE films were investigated by X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS, respectively). For the UPS and XPS measurements, SiO_2/Si wafers were used as substrates. The substrates were cleaned with a boiled acetone solution, followed by multiple rinsing with acetone, isopropyl alcohol, and distilled water. MWPE solutions were spin-coated on the substrates and each sample was mounted on a sample holder. XPS and UPS data were collected in the ultrahigh vacuum condition (Escalab 220IXL). Since MWPE films were conductive enough, these samples did not show undesired charging effects. The thickness of the MWPE films were measured using a surface profiler (Alpha-Step IQ, KLA-Tencor), which was found to be approximately ~100 nm. The MWPE composite films were used as source/drain (S/D) electrodes in pentacene OTFTs and organic complementary inverters; they were also used as catalytic counter electrodes (CCEs) in DSSCs. Detailed device fabrication procedures can be found in our previous reports [18–21]. The current-voltage (*I-V*) characteristics of the OTFTs were measured with an Agilent E5270A precision semiconductor parameter analyzer in ambient air. The *I-V* characteristics of the organic complementary inverters were analyzed using a Keithley 4200 semiconductor characterization system in a N_2-gas filled glove box (H_2O/O_2 < 0.1 ppm). *I-V* characteristics of the DSSCs were investigated using a solar simulator with a xenon lamp (300 W). The power of the simulated light was calibrated to AM 1.5 and 100 mW/cm^2 with a standard Si solar cell. Subsequently, the *I-V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a source meter (Keithley 2400). The charge-transfer resistances related to the CCE and the electrolyte were measured by electrochemical impedance spectroscopy (EIS, from 100 mHz to 100 kHz).

3. Result and discussion

Prior to the fabrication of MWPE composite films, we investigated the atomic compositions of the four different MWCNTs. The XPS spectra in Fig. 1(a) and (b) reveal the oxygen 1s (O 1s) and the carbon 1s (C 1s) core level structures of the MWCNTs, respectively. All the MWCNTs showed typical features of sp^2 hybridization and π-π* transitions; however, significant differences were observed in their atomic compositions [18,24]. As shown in the O 1s core level structures, both TMC 100-05 and TMC 100-10 contain three oxidation states (C—O, C═O, and metal oxide). The O/C atomic ratios of TMC 100-05 and TMC 100-10 are 1.24% and 1.92%, respectively. Once the TMC 100-05 and TMC 100-10 MWCNTs were subjected to chemical/mechanical refining processes, they (i.e. TMC 220-05 and TMC 220-10) exhibited completely different chemical states. TMC 220-05 showed an increased O/C atomic ratio (up to 4.29%), probably because the refining process of TMC 100-05 led to the considerable growth of C—O and C═O oxidation states, while a decrease in the metal oxide impurities was less effective. On the other hand, the O/C atomic ratio of TMC 220-10 decreased (down to 0.08%), which implies that the refining process of TMC 100-10 may not induce oxidization in MWCNTs of large diameter.

Different types of MWPE films were prepared by spin coating their respective MWPE solutions (5000 rpm for 30 s). Hereafter, the four types of MWPE films (according to the diameter and purity of MWCNTs) will be referred to as (1) '100-05' prepared from TMC 100-05 MWCNTs, (2) '100-10' prepared from TMC 100-10 MWCNTs, (3) '220-05' prepared from TMC 220-05 MWCNTs, and (4) '220-10' prepared