Synthetic Metals 159 (2009) 1701–1704

Contents lists available at ScienceDirect

Synthetic Metals

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

# Enhanced optical and electrical properties of PEDOT: PSS films by the addition of MWCNT-sorbitol

Y. Chen, K.S. Kang*, K.J. Han, K.H. Yoo, Jaehwan Kim

*Center for EAPap Actuator, Department of Mechanical Engineering, Inha University, 253 Yonghyun-Dong, Nam-Ku, Incheon 402-751, South Korea*

ARTICLE INFO

*Article history:*
Received 16 April 2008
Accepted 8 May 2009
Available online 24 July 2009

*Keywords:*
Carbon nanotubes
Conducting electrode
Sorbitol
Functionalized carbon nanotube

ABSTRACT

A thin layer of carbon nanotubes (CNTs) presents a strong candidate for application as a transparent conducting electrode and a high frequency Schottky diode. Multiwalled carbon nanotubes (MWCNTs) were modified using nitric acid to form –OH and –COOH groups on the MWCNT surface. Functionalized MWCNTs (FMWCNTs) were further modified using sorbitol molecules. N, *N*′-carbonyldiimidazole (CDI) was utilized as an activating agent for carboxylic acids in a homogeneous one-pot reaction of FMWCNTs in N,*N*-dimethylacetamide (DMAc). The activated FMWCNTs were mixed with sorbitol and heated up to 60 °C with stirring. Due to the mild conditions and efficiency of the reaction, a large amount of sorbitol molecules were covalently attached with increasing reaction time. The FMWCNTs with sorbitol (FMWCNTSORs) were mixed with poly(3,4-ethylene dioxythiophene):poly(styrene sulphonate) (PEDOT:PSS). The FMWCNTSORs were homogeneously dispersed into PEDOT:PSS solution without any precipitation. The FMWCNTSORs/PEDOT:PSS film showed stronger FTIR absorption peaks in the case of samples reacted for longer time. The UV–vis transmittance and the conductivity of the FMWCNTSORs/PEDOT:PSS film was increased as the reaction time increased. Although the field emission scanning electron microscope (FESEM) surface image of the 2 h reacted FMWCNTSORs/PEDOT:PSS film showed large number of small aggregated particles, only a small number of aggregated particles was found for the sample reacted for 6 h. These results indicate that the appropriate amount of sorbitol molecules on the MWCNT can increase the conductivity and transmittance of the PEDOT:PSS film.



## 1. Introduction

Optically transparent conducting electrodes have been the focus of considerable research due to their application in flat pannel displays and organic light emitting diodes (OLEDs). Flexible displays are expetced to play a major role in the future display industry. Conducting polymers are considered the best candidates for flexible transparent conducting electrodes. Among these polymers, poly(3,4-ethylene dioxythiophene):poly(styrene sulphonate) (PEDOT:PSS) is particularly attractive due to its high conductivity, structural stability, optical transparency, and processibility. Despite its versatile advantages, the conductivity is still a limitting factor for practical application in optoelectronic devices. However, PEDOT:PSS having significantly enhanced conductivity has been developed by the addition of sorbitol [1], glycerol [2], ethylene glycol [3], dimethyl sulfoxide [4], meso-erythritol [4], and poly(ethylene glycol) [5], respectively, to the PEDOT:PSS solution prior to film casting. HCl treatment [6] and rinsing in water [7] also increased the conductivity.

Carbon nanotubes (CNTs) have attracted much attention due to their excellent strength and high electrical and thermal conductivity. They also allow versatile versitile surface modification. However, difficulties in making a stable dispersion in a liquid system due to CNT interactions and entanglements has resulted in their poor processibility. Effective reinforcement or electrical conductivity in polymer composites can be achieved by establishing a proper dispersion and good interfacial bonding between the CNTs and the polymer materix. A proper dispersion can be achieved via surface modification of the CNTs. The chemical oxidation of CNTs with $HNO_3$, $O_3$, $OsO_4$, $RuO_4$, or $KMnO_4$ provides oxygen containing groups, such as carboxylate groups, ether groups, and –OH groups, on the ends and surfaces of the nanotubes. Following the succesful incorporation of oxygen containing groups on CNTs, other studies reported further modification performed using silanization [8], (3-aminopropyl)-triethoxysilane and biomolecules [9], and 1,2-bis-(10,12-tricosadiynoyl)-sn-glycero-3-phosphoethanolamine phospholipid [10].

Research on CNT-polymer mixtures to complement indium tin oxide (ITO) could provide a new class of transparent conducting materials for certain applications such as OLEDs and solar cells. One of the most important advantages of CNT-polymer composites is superior flexibility with respect to ITO. Another important

* Corresponding author. Tel.: +82 32 874 7325; fax: +82 32 832 7325.
*E-mail address:* kkang@inha.ac.kr (K.S. Kang).

0379-6779/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2009.05.009

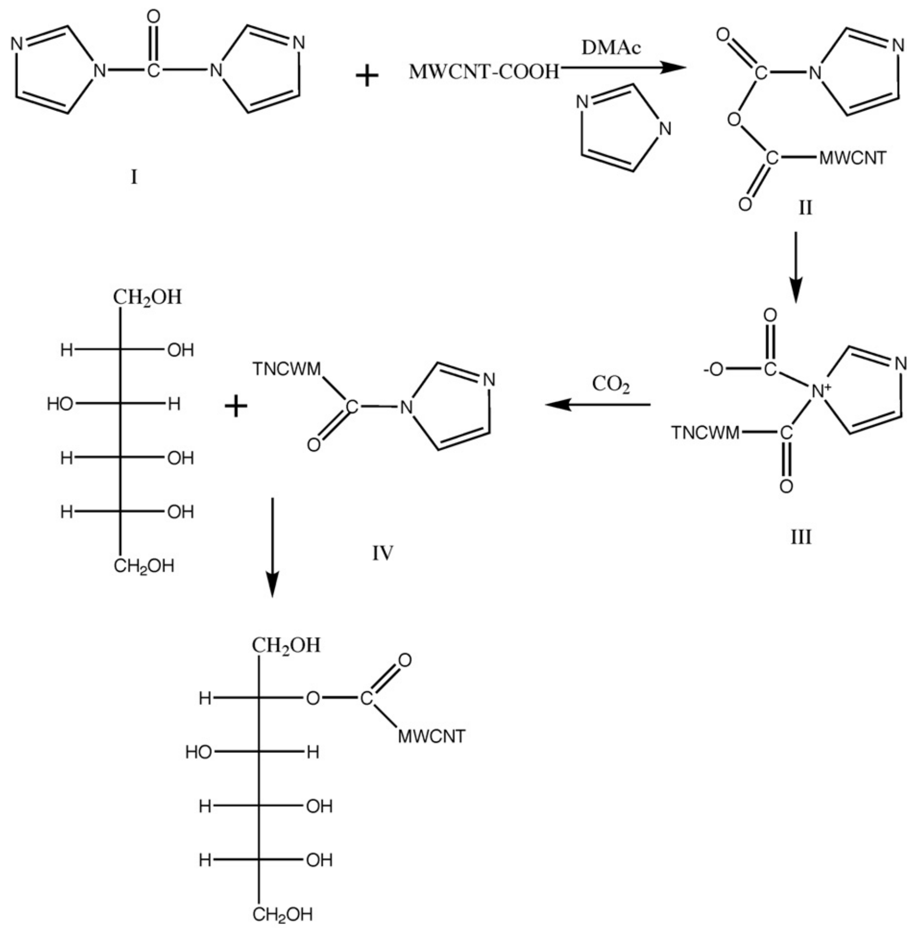


**Fig. 1.** Synthetic process of the FMWCNT and sorbitol. The –COOH groups were activated by the CDI molecules and reacted with –OH groups of the sorbitol molecules.

consideration is that CNTs are a naturally abuntant material compared with indium. In a previous study, transparent, conductive, and flexible CNT films were fabricated, and a smooth surface was achieved through PEDOT:PSS passivation [11]. A double layer conductive transparent electrode using CNTs and PEDOT:PSS was also fabricated on a transparent polyethylene terephthalate (PET) film [12,13]. Another work investigated CNTs incorporated into a PEDOT:PSS mixture using polyethyleneimine and gum arabic, which acts as a surfactant for better dispersion [14,15].

In this investigation, we report two-step modification processes of the MWCNT including surface functionalization with $HNO_3$ and covalent bond formation with sorbitol using CDI as an activating agent. FTIR spectra of the Multiwalled carbon nanotubes (MWCNTs)ORs, UV–vis transmittance spectra, electrical resistivity, and surface FESEM images of PEDOT:PSS films mixed with Functionalized MWCNTs (FMWCNTSORs) were also reported in this paper.

## 2. Experimental

PEDOT-PSS, DMAc, CDI, sorbitol, and MWNTs were purchased from Sigma-Aldrich and used without further purification. Concentrated nitric acid (60%) was obtained from DC Chemical Co., Ltd.

For the sample preparation, 500 mg of MWCNTs was dispersed in 100 ml of concentrated nitric acid using an ultrasonic device (Fisher Scientific, FS30H). The dispersion was refluxed at 90 °C for 24 h. The resulting solution was filtered using a nanofilter having a pore size of 200 nm. The remaining solid was repeatedly washed using deionized water until the pH reached 7. The FMWCNTs were dried in an oven at 80 °C for 24 h.

FMWNTs (25 mg) were dispersed in 50 mL of DMAc. CDI (95 mg) was added to the FMWCNTs solution. The mixture was stirred for 24 h at 60 °C to activate the carboxylic acids attached to the FMWCNT surface. A sufficient amount of sorbitol (212 mg, 2:1 molar ratio with respect to CDI) was dissolved in DMAc solvent and added to the reaction mixture. The mixture was stirred for various times at 60 °C. The reactant was filtered and washed with acetone and DI water repeatedly to completely remove residual CDI and sorbitol. The resulting product was dried in an oven for 24 h at 80 °C. Finally, the FMWCNTSORs were obtained.

FMWCNTSORs were dissolved in DMAc solvent. A fixed amount of FMWCNTSORs was added to 3 g of PEDOT:PSS. The solutions were spin-coated onto a glass substrate using a spin-coater (Laurell, EDC2-100) and dried in an oven for 24 h at 80 °C. UV–vis spectra and conductivity were measured using an HP 8452A UV–vis spectrometer and a CMP-200 probe station equipped with a Precision Premier II ferroelectric system (Radiant Technology INC), respectively. The solutions were spin-coated onto a silicon wafer to investigate the FESEM surface morphology. FTIR spectra for the sorbitol and FMWCNTSORs were recorded using a Bio-RAD FTS-3000 IR spectrometer. Surface images of the films were obtained using a HITACHI S-4000 FESEM.

## 3. Results and discussion

The MWCNTs were functionalized using HNO3 to make –OH and –COOH groups on the surface of the MWCNTs. The –COOH