Optik 157 (2018) 435–440

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Original research article

# Synthesis and characterization of transparent conducting SWCNT/PEDOT: PSS composite films by spin coating technique

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ARTICLE INFO

*Article history:*
Received 26 May 2017
Received in revised form 19 October 2017
Accepted 28 October 2017

*Keywords:*
PEDOT:PSS
SWCNT
Conductivity
Transparency
Composite
Figure of merit

ABSTRACT

Transparent conducting carbon nanotube (CNT)/Poly (3,4 ethylenedioxy thiophene) poly(4-styrenesulfonate) (PEDOT:PSS) composite films are prepared by spin coating technique. The loading rate of CNTs in the host polymer is optimised to enhance the conductivity of the polymer without compromising the transparency of PEDOT:PSS. The effect of single walled CNT (SWCNT) loading on the transparency and conductivity are systematically studied using UV–vis-NIR Spectrophotometry and Hall Measurement. The structural features of the polymer are found to be unaffected by the incorporation of CNTs through XRD, FTIR and Raman analysis. The SWCNT form a network with the PEDOT:PSS matrix which enhances the conductivity of host. A six fold increase in the electrical conductivity of PEDOT:PSS is observed upon incorporation of 0.35 wt% of SWCNT when the figure of merit of the transparent conductor is reduced by $10^2$.



## 1. Introduction

The demand for flexible, organic electronics gave impetus for the search of polymer materials which could be of use in solar cells, sensors, light emitting diodes and in advanced display devices. Polymers take the fore front in flexible electronics applications due to their high flexibility and light weight in addition with good thermal and chemical stability. To be of use optoelectronic applications especially in solar cells polymers with good transparency in the visible region along with reasonably good electrical conductivity are preferred [1]. Polymers such as polyaniline, polypyrrole polythiephene, Poly (3,4ethylenedioxythiophene) (PEDOT):poly(styrenesulfonate) (PSS) have received considerable attention for utilization of transparent conductors and makes it a possible replacement for indium tin oxide to lower the cost of device. PEDOT is a conducting polymer which is insoluble in water thereby possessing a major drawback for solution processing [2]. The solubility problem of PEDOT could be overcome by introducing a water-soluble polyelectrolyte, poly(styrenesulfonic acid) (PSS), which serves as a charge-balancing counter ion agent and helps to disperse PEDOT segments in water during polymerization. The resulting poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) dispersion possesses superior colloid stability. It is a very stable and easy-to-process dark blue dispersion in which the two polymers are electrostatically bound. PEDOT:PSS possesses outstanding advantages such as high transparency in the visible range, thermal stability, especially the tunable conductivity achieved by secondary doping [3–5].

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https://doi.org/10.1016/j.ijleo.2017.10.174
0030-4026/

**Table 1**
Electrical and Optical properties of PEDOT:PSS and SWCNT/PEDOT:PSS thin films.

| No. of spin cycle/Loading rate | Bulk concentration (/cm$^3$) | Mobility (cm$^2$/Vs) | Sheet resistance (Ω) | Conductivity (S/ cm) | Resistivity (Ωcm) | Transmittance at 855 nm (%) |
|---|---|---|---|---|---|---|
| PEDOT:PSS/One cycle | $1.709 \times 10^{14}$ | $9.947 \times 10^{1}$ | $1.224 \times 10^{7}$ | $2.723 \times 10^{-3}$ | $3.672 \times 10^{2}$ | 78 |
| PEDOT:PSS/Three cycles | $4.189 \times 10^{17}$ | 6.545 | $5.692 \times 10^{4}$ | $4.392 \times 10^{-1}$ | 2.277 | 67 |
| SWCNT/PEDOT:PSS one cycle/0.25 wt% | $1.653 \times 10^{15}$ | $4.80310^{1}$ | $2.621 \times 10^{6}$ | $1.27210^{-2}$ | $7.862 \times 10^{1}$ | 71 |
| SWCNT/PEDOT:PSS three cycles/0.25 wt% | $1.126 \times 10^{17}$ | $1.789 \times 10^{1}$ | $7.744 \times 10^{3}$ | 3.228 | $3.098 \times 10^{-1}$ | 60 |
| SWCNT/PEDOT:PSS one cycle/0.35 wt% | $1.477 \times 10^{17}$ | $1.21 \times 10^{-1}$ | $8.736 \times 10^{3}$ | 2.862 | $3.494 \times 10^{-1}$ | 68 |
| SWCNT/PEDOT:PSS three cycles/0.35 wt% | $3.430 \times 10^{17}$ | $6.094 \times 10^{1}$ | $7.466 \times 10^{3}$ | 3.348 | $2.987 \times 10^{-1}$ | 66.8 |
| SWCNT/PEDOT:PSS two cycles/0.45 wt% | $2.782 \times 10^{17}$ | $3.362 \times 10^{1}$ | $2.225 \times 10^{4}$ | 1.498 | $6.675 \times 10^{-1}$ | 64.6 |
| SWCNT/PEDOT:PSS three cycles/0.45 wt% | $1.067 \times 10^{19}$ | $1.465 \times 10^{1}$ | $7.985 \times 10^{2}$ | $2.505 \times 10^{1}$ | $3.993 \times 10^{-2}$ | 55.2 |

The stable and water soluble PEDOT:PSS is found to possess very low conductivity, the character which shields it from being a prospective candidate for organic application. The low conductivity is attributed to the discontinuous nature of the polymeric structure which has poor interconnected grains [6–9]. Hence the conductivity of PEDOT:PSS is to be increased and remains as a challenge. In the present work, an attempt has been made to enhance the electrical conductivity of PEDOT:PSS by introducing a network which will induce a change in the pristine structure of the polymer and interlink the discontinuous structures of the polymeric chain. The carbon Nanotube exhibited high conductivity, transparency and the photovoltaic characteristics are superior compared to the ITO [10,11]. Carbon nanotube is known for its electrical conductivity and thermal conductivity. In the work, it is proposed to synthesis SWCNT/PEDOT:PSS composite film to enhance the electrical conductivity without much compromise in optical transparency and hence to analyze the characteristics of the composite film for its propable application as transparent conductors in solar cell applications.

## 2. Synthesis and deposition of SWCNT/PEDOT:PSS composite film

SWCNT/PEDOT:PSS composite film is prepared by spin coating technique as described elsewhere [12]. The w/v% of SWCNT that is incorporated into PEDOT:PSS is optimized to get desired optical and electrical characteristics (Table 1). The as-deposited film is vacuum annealed for an hour at 100 °C. To analyze the effect of SWCNT incorporation in PEDOT: PSS, pristine PEDOT:PSS film is deposited under the same conditions and characterized. PEDOT: PSS (1.3 wt% dispersion in $H_2O$, Aldrich) and Single Walled Carbon Nanotube (SWCNT, carbon >90% ≥70% 0.7–1.3 nm diameter, Aldrich) are used without further purification.

Systematic analysis on the characteristics of deposited films is carried out. X-Pert Pro PANalytical X-ray diffractometer (Bragg Brentano configuration, Cu Kα), Raman spectrometer (LABRAM,Horiba Jobin Yvon) and High resolution transmission electron microscope (JEOL JEM-2100) are used for the microstructural characterisation of the material. Functional groups present in the material are identified using Fourier transform infrared analyzer (Shimadzu, IR affinity-1). The optical properties of the films are analysed using UV–vis-spectrophotometer (JASCO, V-670). Electrical characteristics of films are analyzed using Hall measurement system (Ecopia, HMS-3000).

## 3. Results and discussion

### 3.1. Structural properties

The X-ray diffraction patterns of pristine PEDOT:PSS film, SWCNT and SWCNT/PEDOT:PSS composite film are shown in Fig. 1. No characteristic diffraction peaks are observed in the case of PEDOT:PSS film thereby indicating the amorphous nature of the polymer. A prominent peak observed in Fig. 1b corresponds to (002) plane of graphitic carbon, which confirms the crystalline nature of SWCNT. The XRD pattern of SWCNT/PEDOT:PSS composite film resembles as that of pristine PEDOT:PSS which indicates the absence of covalent interaction between PEDOT:PSS and SWCNT phases[13].

The Raman spectrum of PEDOT:PSS (Fig. 2a) features Raman bands corresponding to the vibrations of C—C bonds in addition to the bands due thiophene rings in the polymer. The prominent band at 1441 cm$^{-1}$ is attributed to $C_\alpha{=}C_\beta$ symmetric vibrations. $C_\alpha{=}C_\beta$ asymmetric stretching produces peak at 1507 and 1568 cm$^{-1}$ respectively which corresponds to thiophene rings in the middle and end of the polymer chain. Occurence of Raman bands at 1258 and 1369 cm$^{-1}$ are co-related to inter-ring stretching deformations of $C_\alpha{=}C_\alpha$ and $C_\beta{=}C_\beta$ respectively. The characteristic vibrational feature of the conducting polymers are retained upon doping with SWCNT in addition with the absence peaks representing of optically active phonon modes of graphite ($E_{2g}$) at 1592 cm$^{-1}$ [14].