Applied Surface Science 277 (2013) 128–133

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Optimizing processes of dispersant concentration and post-treatments for fabricating single-walled carbon nanotube transparent conducting films

Jing Gao, Wen-Yi Wang, Li-Ting Chen, Li-Jun Cui, Xiao-Yan Hu, Hong-Zhang Geng*

State Key Laboratory of Hollow Fiber Membrane Materials & Membrane Processing, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China

ARTICLE INFO

Article history:
Received 12 November 2012
Received in revised form 3 April 2013
Accepted 4 April 2013
Available online 10 April 2013

Keywords:
Single-walled carbon nanotubes
Transparent conducting film
SDBS
Nitric acid
Thionyl chloride

ABSTRACT

This study evaluated the effect of sodium dodecyl benzene sulfonate (SDBS) as dispersant for the dispersion of purified single-walled carbon nanotubes (SWCNTs) in water in terms of dispersibility dependence on electrical conductivity of SWCNT transparent conducting film (TCF) performance. SWCNT TCFs were prepared by different proportions of CNTs/SDBS solution to find out the optimum SDBS concentration according to the film resistance of pristine and after post-treatment by nitric acid. TCFs fabricated with the aqueous solution by the ratio of CNTs/SDBS 1:5 gave the lowest sheet resistance and the highest transmittance. The TCFs were then further treated with thionyl chloride to improve their conductivity. Low sheet resistance (86 Ω/□, 80%*T*) was achieved. The dispersion condition of CNTs/SDBS aqueous solution was characterized by field-emission scanning electron microscopy, while the X-ray photoelectron spectroscopy and Raman spectroscopy confirmed the dispersion and doping mechanism treated with nitric acid and thionyl chloride.

1. Introduction

Transparent conducting films (TCFs) have been widely used in applications such as field emission displays [1,2], thin film transistors [3], organic light emitting diode [4], solar cells [5] and etc. The main conducting material currently widely used is indium-tin oxide (ITO) which is brittle, expensive, and harmful to the environment. Carbon nanotubes (CNTs) have been regarded as one of the most potential candidates to replace ITO due to its superior and unique optical, electrical, and mechanical properties [6,7].

In order to achieve excellent CNT films with rather low resistance and high transmittance, many factors should be considered. As singled-walled CNTs (SWCNTs) are easily bundled together due to their strong van de Waals interaction, SWCNTs should be dispersed in aqueous solution or organic solvent to achieve microdispersion or nanodispersion [8]. Many dispersants are evaluated such as ambipolar dispersant-Nafion which disperses SWCNTs in a bisolvent containing water and 1-propanol [9], anionic dispersant (sodium dodecyl sulfate, SDS) [10], cationic dispersant (cetyl trimethylammonium bromide, CTAB), nonionic dispersant (polyvinylpyrrolidone and Tween 60). Surfactants assist SWCNTs in dispersing in aqueous media as their hydrophobic tails attached on the surface of SWCNTs while their hydrophilic heads drag them to water, in which the amount of surfactants should be optimized since an excess of surfactants may deteriorate the balance of dispersant/SWCNT solution [11]. Among all these dispersing agents, sodium dodecylbenzene sulfonate (SDBS) is identified as the more economic, environmental and effective agent. Despite a number of SDBS dispersing SWCNTs researches have been carried out for individual CNT dispersion for spectroscopic studies and electrical properties [12], the extent of SDBS dispersing CNTs applied to fabricating TCFs is still necessary to obtain a fundamental understanding of its effect on the dispersion of SWCNTs and the electrical properties of SWCNT networks [13].

Nevertheless, when SWCNT thin films are obtained, the remaining dispersants attached on the surface and between the conjunctions of CNTs would degrade the performance with high resistance. Several approaches have been suggested that the electrical conductivity could be improved without decreasing transmittance by treatment with HNO_3 [9,14], immersion in $SOCl_2$ [15] or doping with alkali metals (Li, Na, K) and halogen groups (Cl, Br, I) to produce n-type and p-type doped SWCNTs, respectively [16,17].

In this work, a multistep to optimize the processing of TCFs were carried out containing dispersing SDBS in 0.3 mg/ml SWCNTs aqueous solution with SDBS concentrations of 1.5 mg/ml, 3 mg/ml, and 6 mg/ml, respectively. After sonication and centrifugation, the supernatant were sprayed on heating polyethylene terephthalate

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* Corresponding author. Tel.: +86 22 8395 5812; fax: +86 22 8395 5055.
E-mail addresses: genghz@tjpu.edu.cn, ghzh88@sohu.com (H.-Z. Geng).

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http://dx.doi.org/10.1016/j.apsusc.2013.04.012

(PET, with high transmittance in visible region) substrate to obtain TCFs [18]. The main purpose of this paper aimed at finding the optimum of CNTs/SDBS (C/S) concentration according to film resistance and improving film conductivity by treating them with nitric acid and thionyl chloride to obtain a simple and effective process of fabricating TCFs and a fundamental understanding of SDBS effect on the dispersion of SWCNTs and the electrical properties of SWCNT networks. It finally came to the conclusion that films fabricated with CNTs/SDBS 1:5 solution leaded to a better dispersion and lower resistance characterized by four-point probe method (Keithley 2700 multimeter) and high transmittance measured by UV–vis spectrophotometer (TU-190). Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was conducted to reveal surface morphology of TCFs. Then a combination of Raman spectroscopy (DXR), X-ray photoelectron spectroscopy (XPS, K-alpha), and energy-dispersive X-ray analysis (EDX) were conducted to investigate the mechanisms of nitric acid and thionyl chloride interactions with SWCNT networks.

2. Experimental

2.1. Dispersion of SWCNTs and fabrication of TCFs

Highly purified arc discharge SWCNTs (purity 96 wt%) purchased from Iljin Nanotech Co., Ltd. were dispersed in deionized water with a concentration of 0.3 mg/ml using SDBS as dispersant with different mixing mass ratios of SDBS/CNTs ranging from 5:1, 10:1, and 20:1, respectively. The solution was sonicated in a sonic bath at 150 W for 10 h and followed by centrifugation at 10,000 × *g* for 10 min. The 80% supernatant was carefully decanted and fed into an air brush pistol (GUNPIECE GP-1). PET substrate was sonicated with acetone and alcohol each for 5 min, rinsed with deionized water, dried in a dry oven and irradiated with a 360 nm monochromatic UV light source (Power 1000 W) for 4 min with a distance of 5 cm [19]. The supernatant in the air brush was directly sprayed onto a heating PET substrate (110 °C) at a constant spray velocity to form a series of different thickness of SWCNT thin films.

2.2. Post-treatment

The sprayed TCFs were then rinsed in deionized water for several times to remove SDBS attached on SWCNTs and dried at 80 °C for 10 min followed by immersion in 12 M nitric acid for 1 h and then rinsed with plenty of water to wash off residual nitric acid and dried again. Finally, TCFs were soaked in thionyl chloride for 30–40 min, and dried.

2.3. Characterization

Transmittance of films was measured by UV–vis spectrophotometer at the wavelength of 400–800 nm. Sheet resistance of pristine and post-treated films was carried out using four-point probe method in sequence. FE-SEM uncovered the extent of dispersion by revealing the surface morphology of TCFs, while Raman spectroscopy with laser excitation energy of 532 nm and 633 nm, XPS and EDX were conducted to investigate the mechanisms of nitric acid and thionyl chloride interactions with SWCNT networks.

3. Results and discussion

Fig. 1 summarized the TCF performance with the sheet resistance versus transmittance at 550 nm with different film thicknesses. The film thickness was increased and controlled by the number of sprays. It showed that the conductivity of TCFs decreased dramatically with increasing SDBS/CNTs mixing ratios in aqueous solution in the graph. SWCNT films have optical transmittance due to the sparse structure of its network, transmittance of water-rinsed and HNO_3-treated films have been measured, there is negligible change in the transmittance in the visible region. According to our study, the fact that the trend of conductivity changed with different amount of SDBS was subject to the extent of dispersion. As for the same films treated with nitric acid, the trends of film sheet resistance changed independent of C/S mixing ratios that C/S with 1:5 resulted in the best film performance compared to C/S with 1:10 and C/S with 1:20. The resistance changing with transmittance presented a similar trend after acid treatment. Much higher ratio of C/S was also tried, it was difficult to obtain well dispersed SWCNT solution due to the hydrophobicity of CNTs, and almost all of CNTs were precipitated after centrifugation resulting in such a big waste. So a C/S mixing ratio of 1:5 was chosen to be an optimum for low sheet resistance and high transmittance both for water and nitric acid treatment.

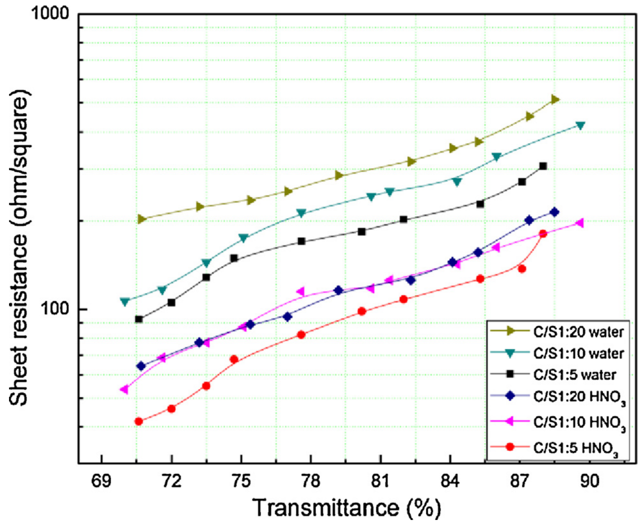

Fig. 1. Sheet resistance–transmittance curves at 550 nm for various pristine TCFs with different mixing ratios of C/S aqueous solution and treated with nitric acid. Each curve contains ten data points from films with different numbers of sprays by the same SWCNT solution.

The degree of dispersion of SWCNTs with SDBS and the bundle size were illustrated from FE-SEM images in Fig. 2(a–c). As described in the previous paragraph, after centrifugation, most of SWCNTs precipitated, leaving supernatant presenting light black for the C/S 1:5 solution, however, there were few residues for the C/S 1:10 and the C/S 1:20 solution, so SWCNTs were easily to dissolve in C/S 1:10 and the C/S 1:20 solution rather than C/S 1:5 solution. The high quality of SWCNT dispersion solution is preferred to individual or small bundle of SWCNTs in solution rather than SWCNT concentration. The quite uniform and small bundles in SEM images by the C/S 1:5 solution reflected the best dispersion of SWCNTs. The extent of dispersing SWCNTs plays an important role in film transmittance, the individual or small bundle of SWCNTs lead to less light absorbing achieving high transmittance. It can clearly explain the trend of resistance-transmittance curves in Fig. 1 that better dispersion reduced absorbance of light resulting lower resistance with high transmittance. The white dots in the images indicated SDBS residues and impurities. TCFs treated with nitric acid demonstrated that most of the SDBS residues were removed and the curled bundles became flattened compared with the pristine SWCNT films, as shown in Fig. 2(d–f). The removal of insulating SDBS on the surface and between SWCNT networks increased the conductivity of the SWCNT films.

Fig. 3 showed a schematic of SDBS dispersing SWCNTs in aqueous solution and removed by nitric acid. As presented in Fig. 3(a) the