Materials Letters 128 (2014) 310–313

Contents lists available at ScienceDirect

Materials Letters

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

Self-assembled transparent conductive composite films of carboxylated multi-walled carbon nanotubes/poly(vinyl alcohol) electrospun nanofiber mats

Zhaoqiang Ding [a], Yanping Zhu [a], Christopher Branford-White [b], Kan Sun [a], Syeda Um-i-Zahra [a], Jing Quan [a], Huali Nie [a,c,*], Limin Zhu [a,*]

[a] College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China
[b] Institute for Health Research and Policy, London Metropolitan University, London N7 8DB, UK
[c] National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 201620, PR China

ARTICLE INFO

Article history:
Received 18 March 2014
Accepted 25 April 2014
Available online 5 May 2014

Keywords:
Transparent conductive composite film
Self-assembled
Carboxylated multi-walled carbon nanotubes (MWCNTs-COOH)
Nanofiber

ABSTRACT

Carboxylated multi-walled carbon nanotubes (MWCNTs-COOH)/poly(vinyl alcohol) (PVA) nanofiber mats were fabricated using electrospinning. Due to the hydrophilic and swelling properties of the nanofibers, a transparent film was generated by self-assembly when the nanofibers were immersed in water. The composite film with MWCNTs-COOH fraction 8.76 wt% exhibits electrical conductivity of 1.8×10^{-4} S/cm, while maintaining 166.98 MPa tensile strength and 61% optical transmittance. The method reported here is simple and feasible for large scale production of CNTs based composite films.

1. Introduction

Carbon nanotubes (CNTs) have effective mechanical, thermal and electronic properties and have been applied in various aspects of nanotechnology, electronics, optics and other fields [1]. These characteristics make them ideal candidates, as a filler to develop new composites that are flexible in terms of being light, with stable mechanical, electrical or thermal properties. CNTs-filled composites have a wide range of applications such as chemical sensors, gas storage materials and transparent electrodes [2–4]. Applications of CNTs-based transparent conductive film do not necessary require high conductivity, for example, electromagnetic interference shielding and electrostatic charge mitigation can be achieved by coating with lower conductivity materials [5]. Currently, many fabrication technologies, such as transfer printing, solution casting, dip-coating, direct CVD growth, and layer-by-layer assembly [6–10], have been used to fabricate CNTs/polymer transparent conductive films. However there remains doubt relating to consistency and uniformity of the composites especially fabrication of the CNTs/polymer composites with a uniform CNTs dispersion and orientation of CNTs [11]. Large scale fabrication is not easy due to use of various potentially toxic organic solvents [12]. This drawback provides an opportunity for further investigations to be undertaken that will provide a new platform for the fabrications of new CNTs based composites that address the above issues. Here we demonstrate a two-step approach involving electrospinning followed by swelling in water to fabricate carboxylated multi-walled carbon nanotubes (MWCNTs-COOH) composite films with poly(vinyl alcohol) (PVA). The films obtained by this approach possess several characteristics such as enhanced mechanical properties, electrical conduction and optical transparency. This two-step approach is simple, less time consuming and environmentally friendly.

2. Experimental procedure

The first phase involved electrospinning aqueous MWCNTs-COOH/PVA obtained by dispersing MWCNTs-COOH in PVA using ultrasonic stirring. Aqueous MWCNTs-COOH (average diameter, 8–15 nm, length 50 μm) were suspended with surfactant sodium dodecyl sulfate (SDS). Concentrations of MWCNTs-COOH were 5, 10, 20, 30, 40 mg/ml and PVA (polymerization of 1750 ± 50 and 99% hydrolyzed) solution (10 wt%) was prepared by dissolving PVA powders in water. Electrospinning solutions were prepared by blending equal volumes of aqueous MWCNTs-COOH and PVA for 45 min ultrasonic stirring. Then the nanofibers were prepared

* Corresponding authors at: College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China.
Tel.: +86 21 6779 2748; fax: +86 21 6779 2655.
E-mail addresses: niehuali@dhu.edu.cn (H. Nie), lzhu@dhu.edu.cn (L. Zhu).

http://dx.doi.org/10.1016/j.matlet.2014.04.165
0167-577X/

using an electrospinning apparatus. MWCNTs-COOH/PVA was used for electrospinning under a flow rate of the polymer solution and an applied voltage of 1.0 ml/h and 13 kV. Following this procedure, an opaque layer of MWCNTs-COOH/PVA pristine nanofiber mat was collected. Interestingly, a transparent and uniform composite film formed immediately after the mat was immersed in water followed by drying under vacuum. Scanning Electron Microscopy (SEM) was used to examine the morphology of the pristine opaque nanofiber mats and the transparent films, whereas Field Emission Scanning Electron Microscopy (FESEM) observed the presence and morphology of the MWCNTs-COOH distributing over the transparent films. Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer Pyris 1 to estimate MWCNTs-COOH weight fraction. Mechanical properties were determined on a C7-80002 Tensile Tester at a speed of 10 mm/min. A Concept 40 Broadband Dielectric Spectrometer was used to test electrical properties. The optical transmittance experiment was carried out with a UV–vis 4802H spectrophotometer.

3. Results and discussion

SEM images of self-assembly process of the transparent film from electrospun nanofibers are shown in Fig. 1(A)–(F). In summary (A) shows micro morphology of the pristine nanofiber mats; (B)–(E) indicate structure changes of the nanofibers swelling with water from beginning to end; (F) shows the compact and non-porous structure of the obtained transparent film after swelling and self-assembly. Fig. 1(G) shows FESEM image of film 40# loading 10.78 wt% MWCNTs-COOH, indicating that MWCNTs-COOH homogeneously dispersed with random orientation within the PVA matrix. It was observed that some MWCNTs-COOH were

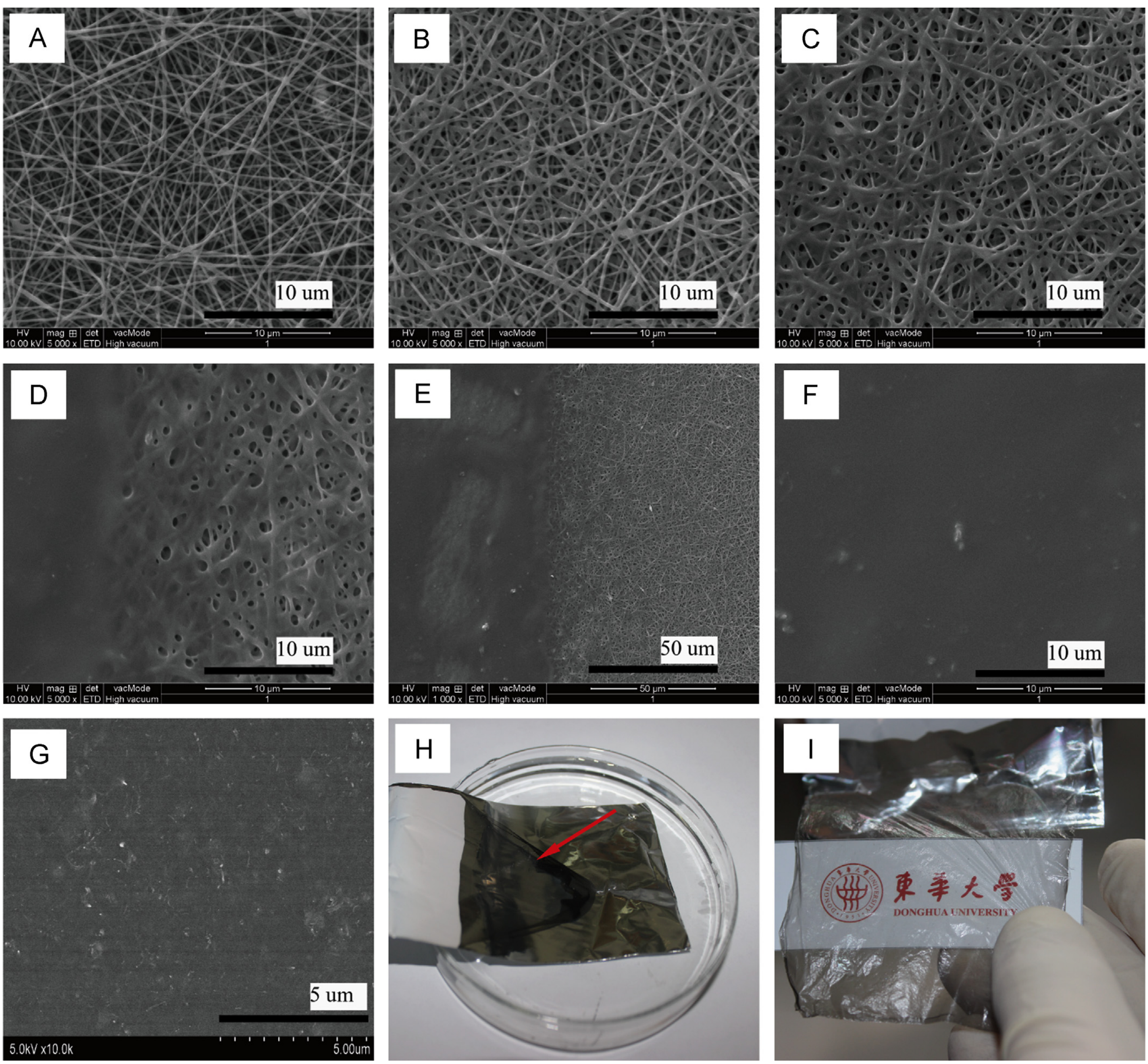

Fig. 1. (A)–(F) SEM images of self-assembly process of the transparent film from electrospun nanofibers; (G) FESEM image of film 40# with 10.78 wt% MWCNTs-COOH; Photographs of (H) the nanofibers' self-assembly in water (the red arrow indicating the transparent film) and (I) the obtained transparent film.