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New insights into the oxidation of single-walled carbon nanotubes for the fabrication of transparent conductive films

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ABSTRACT

Transparent conductive films (TCFs) based on oxidized single-walled carbon nanotubes (SWCNTs) are not typically fabricated because this type of SWCNT includes sp^3 carbon centers, which impede carrier transport. The acidic carbonaceous fragments (ACFs) that are created during oxidative reactions act as dispersing agents, enabling the dispersion of SWCNTs without additives. However, the structure of ACFs prohibits carrier transport in networks; thus removal of ACFs from the SWCNT networks is essential for improving TCF performance. In this work, we used this idea in order to fabricate ACF-free high-performance TCFs based on oxidized SWCNTs. The ACFs were initially used as dispersing agents. They were then dissolved and removed after the formation of a SWCNT network. The functional groups introduced onto the oxidized SWCNTs were mainly distributed across ACFs, whereas the SWCNTs remained unmodified. The removal of the ACFs improved the performances of the TCFs. As the sizes of the unmodified SWCNT bundles decreased, the performances of the oxidized-SWCNT-based TCFs improved (σ_{dc}/σ_{op} = 14.7), providing properties comparable to those of films prepared using a surfactant-stabilized dispersion.

1. Introduction

Carbon nanotubes (CNTs) have attracted enormous interest in a variety of scientific fields due to their unique electrical properties [1]. Transparent conductors based on single-walled carbon nanotube (SWCNT) thin films show promise as replacements for conventional transparent conductive materials, such as indium tin oxide, because SWCNT films may potentially be manufactured using solution processing at low costs and yielding excellent flexibility [2]. Numerous approaches to fabricate SWCNT thin films, including dry deposition [3,4] or solution-based processing, have been reported [5]. In the solution processing, SWCNTs aggregate easily due to intermolecular van der Waals interactions; therefore, it is essential to prepare effective dispersions for a variety of applications [6]. Dispersions of SWCNTs used to fabricate transparent conductive films (TCFs) are usually prepared using a dispersing agent, such as sodium dodecyl sulfate (SDS) [7,8], sodium dodecylbenzenesulfonate (SDBS) [9], or Triton X-100 [10,11]. These methods require excessive amounts of the additive. Moreover, the dispersing agents are insulating, and the incomplete removal of such agents

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can reduce the electrical conductivity through the resulting networks [8]. The preparation of a dispersion of SWCNTs without additives is essential for achieving high-performance TCFs.

SWCNTs may be dispersed in a liquid media without additives through the introduction of functional groups [6]. Oxidation of nanotubes provides a good method for doing so. Reactions with strong acids, ozone, or other oxidizing agents generate oxygen-containing functional groups, such as carboxylic, hydroxyl, and carbonyl groups [12,13]. Improved interaction between oxidized nanotubes and solvent molecules yields enhanced dispersibility [14]. The degree of oxidation may potentially be increased to fabricate high-performance CNT networks from individual nanotubes; however, oxidative reactions can also cut the SWCNTs [15,16] and decrease their electrical conductivity due to the presence of defects [17]. These drawbacks and the poor performances of oxidized SWCNTs, as reported in the literature [18,19], have removed oxidative reactions from the list of approaches typically used to fabricate TCFs [20].

During an oxidative reaction, acidic carbonaceous fragments (ACFs) are released from the highly attacked sites of the nanotubes [21–23]. ACFs have an aromatic backbone with polar functional groups. ACFs easily adhere to the CNTs and improve the dispersibility of the oxidized SWCNTs in liquid media [22]. Electrically insulating ACFs in CNT networks significantly increase the junction resistance between nanotubes, which reduces the electrical conductivity of a SWCNT network. Previous study reported that the functional groups present in oxidized CNTs mainly attached to ACFs [21]. The removal of ACFs after film formation, therefore, enables the fabrication of networks that are more electrically conductive than those found in ACF-containing films. The fabrication of TCFs based on oxidized SWCNTs without ACFs has not been reported previously.

Here, we fabricated high-performance TCFs based on oxidized SWCNTs through the selective dissolution of ACFs after formation of films. ACFs were utilized as dispersing agents for the preparation of SWCNT networks. The ACFs were removed to fabricate ACF-free films. The properties of oxidized SWCNTs were investigated to characterize the influence of the removal of ACFs on the chemical nature and performance of the resulting TCFs. The effects of oxidation on the size of bundles, length of the oxidized SWCNTs, chemical nature, and performance of the TCFs were analyzed.

2. Experimental

2.1. Materials

SWCNTs (synthesized by the CVD method, outer diameter < 2 nm, purity > 95 wt%, initial length: 5–30 μm) were purchased from Chengdu Organic Chemicals. Sulfuric acid (H_2SO_4, concentrated, 95%), nitric acid (HNO_3, 14.2 M) and sodium hydroxide (NaOH, pellet, 97% purity) were purchased from Daejung (Korea). SDS (purity ⩾ 98.5%) was purchased from Sigma–Aldrich. All materials were used without further purification.

2.2. Oxidation of SWCNTs

As-received SWCNTs (denoted A-SWCNTs) were oxidized by HNO_3 solely (denoted N-SWCNT) or a mixture of H_2SO_4–HNO_3 (v/v = 3/1, denoted M-SWCNT). A 300 mg sample of each A-SWCNTs was added to 90 mL oxidant. The degree of oxidation was controlled by varying the oxidative time: 24, 48, 72, 96, or 120 h for N-SWCNTs (denoted N24, N48, N72, N96, and N120); or 3, 12, 24, 48, and 72 h for M-SWCNTs, respectively (denoted M3, M12, M24, M48, and M72). The reaction was performed at 110 °C for the N-SWCNTs and at 60 °C for the M-SWCNTs. After the reaction, the dispersions were cooled to room temperature, filtered, and rinsed with deionized water until the filtrate was colorless and neutralized. The obtained neutralized oxidized SWCNTs were dried under vacuum at 60 °C for 2 days.

2.3. Preparation of the SWCNT dispersion

A 5 mg sample of the dried oxidized SWCNTs was weighed and added to 100 mL deionized water. Mixtures were sonicated for 20 min using a horn-type sonicator operated at 200 W (Sonopuls HD, 20 kHz) with an amplitude of 40%. After sonication, dispersions were centrifuged at 12,000 rpm for 20 min (Heraeus Megafuge 16, 230 V) to remove aggregates and other impurities. The final dispersions used for further experiments were obtained by decanting the top ~80% of the supernatant. As a reference, a SWCNT dispersion in a 0.5 wt% SDS aqueous solution was prepared through process described above.

2.4. Fabrication of the SWCNT TCFs

TCFs were fabricated using the vacuum filtration over an anodic aluminum oxide (AAO) membrane filter (200 nm pore size, 47 mm diameter; Whatman). After filtration, the AAO filter was dissolved using a 3 M NaOH solution bath. The floating free-standing SWCNT thin films were transferred to a glass substrate (Soda-lime glass, Duran). The transferred TCFs then underwent two cycles of heating to 80 °C for 5 min and rinsing with deionized water for 10 s to remove remnant NaOH. The conductivity of the TCFs was improved by dipping the films in 8 M nitric acid for 30 min, followed by drying at 80 °C for 5 min. The SWCNT TCFs fabricated using dry transfer methods were prepared as a comparison sample. To confirm the practical feasibility of flexible SWCNT TCFs, the nanotube networks were transferred to a polyethylene terephthalate (PET) substrate. Same process for removal of remaining NaOH was performed, only controlling the heating temperature to 70 °C to prohibit the glass transition of PET.

2.5. Characterization

Washings with base solution were performed in order to measure the relative amount of ACFs in the oxidized SWCNTs. 10 mg of each oxidized SWCNT was added to 10 mL of 3 M NaOH solution and the resulting mixture was stirred for 12 h. After washing, the mixtures were filtered using a polytetrafluoroethylene membrane filter (100 nm pore size,

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