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Inkjet printed transparent conductive films using water-dispersible single-walled carbon nanotubes treated by UV/ozone irradiation

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ABSTRACT

Water-based single-walled carbon nanotube (SWCNT) inks with excellent dispersibility for inkjet printed transparent conductive films were prepared by a simple and versatile UV/ozone treatment. The dispersion stability of the SWCNTs was enhanced by the increased oxygen-containing groups on the SWCNT surfaces which were created by the UV/ozone treatment. After inkjet printing of the ink to obtain transparent conductive patterns, circular rings in which most of the SWCNTs are concentrated at the rim were formed by coffee ring effect. The transparent conducting films were achieved by connecting and stacking the rings; the final films inkjet printed in 40 layers have a sheet resistance of 870 Ω sq^{-1} at 80% optical transmittance in the wavelength of 550 nm.

1. Introduction

Transparent conductive coatings are used in a wide range of applications such as liquid crystal displays, light emitting diodes, transistors, actuators, sensors, organic solar cells, and heated windows [1–6]. Currently, transparent conducting oxides (TCOs) such as indium doped tin oxide and fluorine-doped tin oxide are the most commonly used for such applications. However, major technical issues associated with the use of TCOs as transparent electrodes exist because of inherent limitations such as the complexity of the manufacturing process, high cost, precursor material abundance, and relatively low conductivity. The fabrication of optically transparent and electrically conductive thin films using single-walled carbon nanotube (SWCNT) has attracted significant attention because of its high conductivity (on the order of 10^3–10^4 S/cm) and high aspect ratio (>100) [7–11]. In comparison to traditional TCOs, SWCNT may allow for substantially reduced costs because of the abundance of source material and potentially scalable solution-based fabrication process. In addition, SWCNT films may also offer additional advantages such as flexibility, enhanced carrier injection and tunable electronic properties by chemical treatments.

Various methods have been utilized to fabricate SWCNT-based transparent conducting films, including spin-coating, spraying, casting, transfer printing, and SWCNT solution vacuum filtration [11–14]. A more recent development is the use of inkjet printers in the deposition of SWCNTs onto substrates; this process allows for practical implementation of SWCNT coatings that are scalable, cost effective, and environmentally friendly [15–17]. The preparation of water-dispersible inks is important to the formation of the inkjet printed SWCNT patterns because organic solvents are incompatible with many plastics used as inkjet printing nozzles and flexible substrates. Generally, the nanotubes are dispersed in a solvent with the help of a surfactant. However, surfactant adsorbed on the tube surface greatly affects the electrical properties [18]. Most of the previously described techniques for preparing water-dispersible SWCNT inks without any surfactants have used an acid treatment with a high concentration mixture of HNO_3 and H_2SO_4 to introduce oxygen-containing carboxyl and hydroxyl groups onto the SWCNT surface [13,19]. However, this method not only creates defects in the SWCNT sidewalls, but also decreases the SWCNT aspect ratio because the strong acids cut the SWCNTs into short pieces during the oxidation process, which may degrade the original electrical and mechanical properties of the SWCNT [20].

Ozone treatment is a very simple process in comparison with other surface modification processes because this process can be carried out in an air atmosphere, and the equipment and operating cost are relatively low. This method is also environment-friendly and can easily induce chemical functionality of the CNTs without changing their unique characteristics, and can enhance dispersion stability in various solvents by inducing oxygen-containing functional groups [21–24]. In this study, water-dispersible SWCNT inks were prepared using a simple UV/ozone treatment as an alternative high concentration acid treatment to create the polar functional groups necessary to

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disperse the SWCNT in a mixture solution of distilled water and methanol. The dispersibility of the SWCNT ink was characterized as a function of UV/ozone treatment time and the surface properties of the SWCNT modified by the UV/ozone treatment were systematically investigated. Transparent conductive films were then fabricated using an inkjet printing process to demonstrate the usefulness of the SWCNT ink prepared by the UV/ozone treatment.

2. Experimental details

SWCNTs (ASP-100F, Hanwha Nanotech Co. Korea) were treated with a commercial UV/ozone generator (Model# 42, Jelight Co. USA). This equipment has a high intensity, low pressure mercury vapor UV grid lamp, and generates UV emissions at 185 and 254 nm wavelengths. The SWCNTs were placed in the ozone exposure chamber with a gas mixture of air and ozone (ozone gas concentration: 1000 ppm). The distance between the UV-source and the SWCNTs was 6 mm. The intensity of irradiation at 6 mm from the high-intensity low-pressure vapor Hg lamp was 28 mW per cm^2. The UV/ozone treatment for the SWCNTs was carried out for 30, 60, 90, or 120 min. After the UV/ozone treatment, the oxygen contents of the SWCNTs were determined using an elemental analyzer (EA 1112, CE Instrument). In addition, the surface modification of the SWCNTs was analyzed by Raman spectroscopy (RFS 100/s, Bruker) using ND-YAG laser with an excitation wave length of 1064 nm and X-ray photoelectron spectroscopy (XPS, ESCA 220i, VG Microtech). The XPS spectra were obtained using a monochromatized Al Kα line ($h\upsilon = 1486.6$ eV) in a chamber with a base pressure of 1.33×10^{-6} Pa. XPS samples were prepared by adhering monoliths directly to copper tape. The copper tape was mounted on a sample holder using double-sided adhesive carbon tape. All measurements were performed using an X-ray power of 150 W (15 kV and 10 mA). In the spectrum analysis, The CASA XPS program with a Gaussian–Lorentzian mix function and Shirley background subtraction was employed to deconvolute the spectra. The C 1s spectrum analysis was carried out by fitting a graphite peak shape, 284.5 eV (±0.35 eV energy resolution of the spectrometer at the settings employed) obtained under the same analysis conditions.

The SWCNT inks with various amounts of SWCNTs were prepared by mixing the UV/ozone treated SWCNTs with a mixture of distilled water and methanol in the proportion of 6:4. The ultrasonic dispersion of the SWCNT suspension was then carried out using an ultrasonicator (VCX 750, Sonic & Materials Inc. USA) for 30 min. The dispersibility of the inks was analyzed by multiple light scattering using a near-infrared ray (Turbiscan-lab, Formulaction Inc. USA) at 1 h interval from as-mixed to 1 day later. The zeta-potential of the SWCNT inks was measured using zeta-potential analyzer (ELSZ-1, Otsuka electronics). The viscosity and surface tension of the inks were characterized with a viscometer (LVDV-II + CP, Brookfield Inc. USA) and surface tensiometer (Sigma 701, Chang-Kyung Cor. Korea), respectively.

The inkjet printing was carried out using the ink with a concentration of 2 mg ml^{-1} of SWCNTs and a piezoelectric inkjet printer (DMP 2831, Fujifilm Dimatix Inc.) equipped with multiple nozzles 25 μm in diameter. The glass substrate (30 mm × 30 mm, Paul Marienfeld) was treated by a methanol in ultrasonic bath for 30 min, subsequently washed by distilled water and dried at 50 °C before the inkjet printing. Transparent films with 10 to 40 printing layers were fabricated by printing the SWCNT ink onto the glass substrate at room temperature. The spaces between inkjet printed dots were set at 50 μm by controlling the inkjet printer. The sheet resistance and transmittance of the inkjet printed SWCNT patterns were characterized by four-point probe (CMT-SR2000N, AIT Co., Ltd. Korea) and UV–vis spectrophotometer (Lambda 750, PerkinElmer Inc. USA), respectively.

3. Results and discussion

Fig. 1(A) shows the transmittance of SWCNT inks containing 0.002 wt.% SWCNT as a function of UV/ozone treatment time. The initial transmitted light intensity exhibits a low value, increasing UV/ozone treatment time. This means that the untreated SWCNT or treated for only a short time agglomerates more than those exposed to UV/ozone for longer amounts of time because there is more empty space for light to pass through when the same amount of SWCNTs agglomerates more in the solution. The transmittance of the bare SWCNT ink sharply increased from 18.3% to 35.4% after 24 h. However, the variation in transmittance over the analysis period decreased with increasing UV/ozone treatment time. This indicates that SWCNTs treated with UV/ozone for a long enough time are able to consistently maintain their dispersibility in a mixture solution of distilled water and methanol. Fig. 1(B–D) shows detailed gradation profiles of each sample obtained by hourly scans. Fig. 2 shows the oxygen content of SWCNT as a function of UV/ozone exposure times. It was found that the oxygen concentration of the SWCNTs before and after UV/ozone treatment (for 120 min) was increased from 2.58 wt.% to 12.09 wt.%. These results indicate that the

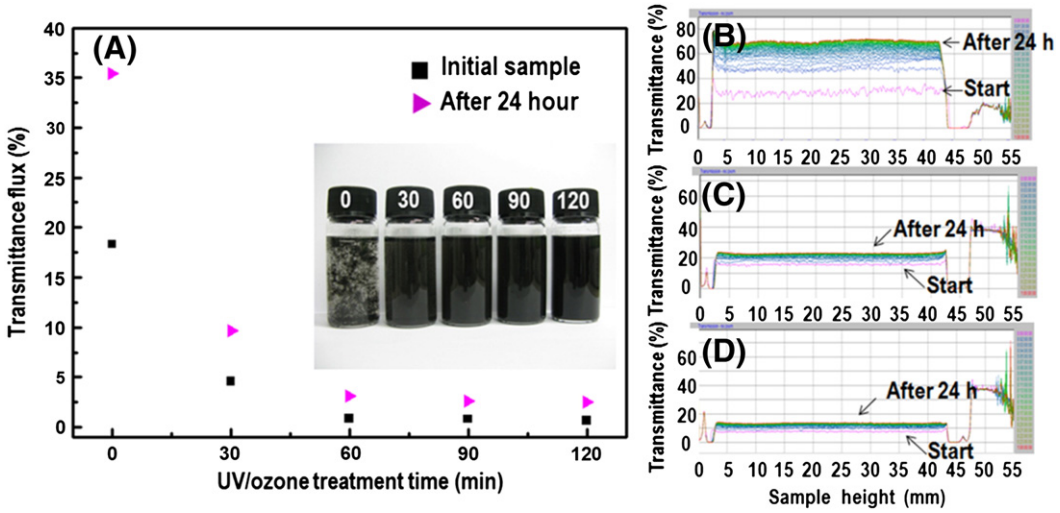

Fig. 1. (A) Graph showing the intensities of light transmitted through SWCNT inks as a function of UV/ozone treatment time and (B–D) detailed gradation profiles obtained via hourly scans; (B) untreated and UV/ozone treated for (C) 60 and (D) 120 min (*Sample height: the position from the bottom of the sample bottle). The inset images of Fig. 1(A) show typical appearances of SWCNT suspensions after 5 days as a function of UV/ozone treatment time.

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