Aerosol-Synthesized SWCNT Networks with Tunable Conductivity and Transparency by a Dry Transfer Technique

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ABSTRACT We demonstrate an aerosol CVD process to dry deposit large-area SWCNT networks with tunable conductivity and optical transmittance on a wide range of substrates including flexible polymers. These SWCNT networks can be chemically doped to reach a sheet resistance of as low as $110 \diameter/\square$ at 90% optical transmittance. A wide application potential of these networks is demonstrated by fabricating SWCNT network-based devices such as a transparent capacitive touch sensors, thin-film transistors (TFTs), and bright organic light-emitting diodes (OLEDs).

KEYWORDS Carbon nanotube, thin film, ITO replacement, transparent electrode, OLED, transistor

Single-walled carbon nanotube (SWCNT) networks are promising for future electronics because of their unique optical and electrical properties.1 Optically transparent conductive electrodes are one of the potential application areas,2 as components of widely utilized electrical devices, such as thin displays and touch sensors. Currently used transparent metal oxides such as indium–tin oxide (ITO) have several drawbacks, including a high refractive index and haze, spectrally nonuniform optical transmission, limited flexibility, restricted chemical robustness, and a depleted raw material supply.3,4 The application potential has induced significant research interest to develop both SWCNT network and other carbon nanostructured coating deposition methods and postprocessing methods. Several recent studies have demonstrated transparent carbon nanotube- or graphene-based electrodes with performance approaching ITO having a sheet resistance, $R_s$, of 280 $\diameter/\square$ at optical transmittance, $T = 80\%$,3 470 $\diameter/\square$ at $T = 87\%$,6 and 220 $\diameter/\square$, 170 $\diameter/\square$,6 and 140 $\diameter/\square$ T = 90%. These processes typically involve several time- and resource-consuming9–12 and potentially detrimental13,14 liquid purification and dispersion steps. We have developed an aerosol CVD-based deposition process that can eliminate liquid processing prior to deposition altogether and therefore decrease the process duration and process-induced damaging of the nanotubes.

SWCNTs were synthesized by the thermal decomposition of ferrocene vapor in a carbon monoxide (CO) atmosphere.15 In this study, two synthesis reactors were used, one being a laboratory-scale reactor consisting of a ferrocene saturator, a water-cooled injector probe, and a heated tube furnace with variable maximum temperature from 800 to 1200 °C. A 300 cm$^3$/min flow of CO was passed through ferrocene powder. This provided the conditions for ferrocene vapor saturation of 0.8 Pa at room temperature. The growth chamber was an alumina tube (with an internal diameter of 22 mm and a length of 550 mm) inserted inside the tube furnace. The flow containing ferrocene vapor was then introduced directly into the high-temperature zone of the ceramic tube reactor through the water-cooled probe (water temperature of 25 °C) inserted 6.5 cm deep into the reactor. An additional CO flow of 100 cm$^3$/min was introduced into the reactor between the water-cooled probe and the reactor tube. The second synthesis reactor that was used in this work was a scaled-up version having a reaction tube of 150 mm in diameter and 1.5 m in length. It was operated at a total CO flow rate of 4 L/min and at a temperature of 880 °C. Ferrocene is thermally decomposed in a temperature gradient formed between the injector probe and the ambient reactor temperature. The decomposition leads to supersaturated conditions that result in iron nanoparticle formation.

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Carbon monoxide gas is decomposed on the formed iron catalyst particles, leading to SWCNT growth. The electrical conductivity of a SWCNT network is limited by highly resistive junctions between SWCNT bundles. Therefore, increasing the length of the SWCNT bundles is expected to decrease the network resistivity because of a smaller number of contacts in series. To study the effect of the SWCNT bundle dimensions on the electrical conductivity of the networks, we prepared samples with different bundle lengths of 1.3 (0.8, 3.3 (1.4, and 9.4 (1.4 µm as shown in Figure 1a. SWCNTs (1.3 and 3.3 µm long) were synthesized in the laboratory-scale ferrocene reactor. On the basis of in situ sampling experiments, we have recently discovered that the length of the SWCNTs is determined by the reactor conditions and the SWCNT growth is terminated at temperatures higher than 945 °C. Therefore, to synthesize short SWCNT bundles (1.3 µm) we utilized a reactor temperature of 1050 °C where the SWCNT growth zone is limited. Longer SWCNT bundles with an average length of 3.3 µm were synthesized at lower temperatures (880 °C) to avoid the inhibition of the CO-disproportionation reaction and SWCNT growth termination. Bundles with an average length of 9.4 µm were synthesized with the scale-up reactor, which was designed to provide a longer residence time for the synthesis of longer SWCNTs. A 1% volumetric fraction of CO2 was mixed at the inlet of the reactors to enhance the catalyst particle activity. Bundle diameter distributions were found to be overlapping (Supporting Information, Figure S4). The bundle length and diameter characteristics were obtained by transmission and scanning electron microscopy (Philips CM200 FEG and JEOL JSM-7500F). SWCNT samples with submonolayer coverage were collected on TEM grids (holey carbon film 400 mesh, Agar Scientific, U.K.). The SWCNT network morphology was also studied by atomic force microscopy (Veeco Dimension 5000, Veeco Instruments).

The SWCNTs form small bundles in the gas phase, which were collected by a membrane filter at the outlet of the reactor to form a SWCNT network (Supporting Information, Figures S2 and S3). The sheet resistance and transmittance were controlled by the network deposition time and by the reactor dimensions and conditions. The synthesized
SWCNT bundles were collected downstream of the reactor by filtering the aerosol through a nitrocellulose membrane filter to form a SWCNT network (Millipore, HAWP, 0.45 µm pore diameter). The networks were transferred from a low adhesion filter to various substrates by a simple room-temperature press transfer process. Usable substrates range from flexible polymers (e.g., polyethylene terephthalate (PET)) to glass, quartz, silicon, and various metals (Supporting Information, Figure S4). A substrate and a SWCNT network on a filter were pressed together with a pressure of 10^3 Pa. No dispersion or purification steps were needed prior to the transfer, thus making the process of film preparation very rapid. The transfer process required less than 15 s to complete (Supporting Information, movie S1). Importantly, by utilizing masks beneath the filter, SWCNT network patterning can be achieved. Flexible electrodes of up to 28 × 28 cm² have been successfully fabricated by this method (Supporting Information, movie S2). Further scaling is possible by simply increasing the filter and substrate sizes. The press transfer method is compatible with roll-to-roll fabrication methods, thus opening up further upscaling potential in industrialized production. UV–vis–NIR optical absorption spectroscopy was performed using a dual-beam spectrophotometer (Lambda 950, Perkin-Elmer). A wavelength of 550 nm was used to characterize the optical transmittance of the films. The optical spectra of as-deposited SWCNTs reveal high-quality tubes (Figure 1b,c). The resistance was found to be strongly dependent on the average bundle length in the SWCNT network (Figure 2a). R_s of the sample containing the shortest bundles (1.3 µm) was 22 kΩ at 90%. The samples with longer bundles (3.3 and 9.4 µm) yielded SWCNT networks with R_s = 2700 and 820 Ω, respectively. The electrical sheet resistance of SWCNT networks was measured using a four-point linear probe and a multimeter (Jandel four-point probe, Jandel Engineering Ltd., England/Agilent 34411, Agilent) from five different locations on the SWCNT network.

To decrease the R_s of the SWCNT networks, we developed a fast postdeposition treatment. The SWCNT network was first densified by drop casting of ethanol and subsequent drying in a laboratory atmosphere. During evaporation, the surface tension of the ethanol compressed the network in
the out-of-plane direction. This increased the network connectivity as the network morphology approached the 2-D limit, as can be observed from the SEM images (Supporting Information, Figure S3). The densification was followed by 60 s of dipping into concentrated HNO$_3$ and deionized water rinsing for 15 s to dope the semiconducting SWCNTs chemically and to decrease the interbundle junction resistance.\textsuperscript{18} The morphology of the liquid-treated SWCNT network is shown in Figure 3b (and in Supporting Information, Figure S4). The improvement in SWCNT conductivity due to ethanol densification and HNO$_3$ treatment is depicted in Figure 2b. Importantly, SWCNT-network $R_s$ dropped to as low as 110 $\Omega/\square$ at $T = 90\%$. For comparison, data for commercially available ITO films on flexible substrates are shown in Figure 2a,b.\textsuperscript{22,23} The chemical treatment with HNO$_3$ has been demonstrated in previous studies, but with significantly longer treatment durations of 15 min, 60 min, and 3 h.\textsuperscript{24–26} In our case, SWCNT films were doped within 1 min, which can be confirmed by optical absorption and Raman measurements. The electrical and optical characterizations were performed 1 h after the postdeposition treatment under ambient conditions. We used ethanol (Etax Aa, Altia, Finland) and 65% HNO$_3$ (65% HNO$_3$, J. T. Baker, Netherlands) in this study.

The suppression of optical transitions shown in Figure 1b suggests a shift in the Fermi level (Supporting Information, Figure S6). The charge transfer was confirmed by Raman spectroscopy. Raman measurements were performed using a 633 nm laser line (LabRAM, Horiba Yvon, France). We observed a significant decrease in Raman intensity and a blue shift in the G (inset of Figure 1c) and G' bands (Figure 1c) in the acid-treated samples, indicating p-type doping of the SWCNTs (detailed discussion in Supporting Information).\textsuperscript{27–29} This p-type doping decreases the resistance of the SWCNT network by enhancing the conduction of semiconducting tubes (Figure 2c).\textsuperscript{26} According to Nirmalraj et al.,\textsuperscript{18} the main role of the acid treatment should be attributed to a decrease in the interbundle junction resistance.
It is worth noting that the electrical conductivity of SWCNT films thicker than a few monolayers can be described by bulk material conductivity laws. The thickness of SWCNT films thicker than a few monolayers can be determined by the concentration and mobility of the charge carriers. The concentration can be altered by the doping of SWCNTs, whereas the mobility in the network is determined by tube-to-tube contacts. Figure 2c demonstrates the method of comparing the relative performance of SWCNT networks with varying parameters by comparing their figure of merit (or coefficient of proportionality $K$).

Transparent SWCNT networks have several application areas where an easy dry transfer can be used to simplify and quicken device fabrication. We have built a capacitive touch (proximity) sensor from a highly ($98\%$, sheet resistance 4 $k\Omega/\Omega$) transparent SWCNT network electrode on a PET substrate, which is connected to a PCB with read-out electronics (Supporting Information, Figure S1) and a touch indicator LED (QT100A, Amtel Corporation). The device is depicted in Figure 3a (Supporting Information, movie S3). The highly conductive SWCNT network coated area exhibits similar touch detection sensitivity to the copper electrode, and the SWCNT electrode can be contacted using silver paint with a low contact resistance of about $50\, \Omega$. Press-transferred SWCNT networks with a density below the metallic percolation threshold can be used as a channel for the TFT. SWCNT networks with a $3.3\, \mu m$ average bundle length were press-transferred onto a boron-doped Si substrate with a $100\, nm$ SiO$_2$ gate dielectric. Source and drain electrodes were lithographically patterned on top of the SWCNT network, which was removed outside of the channel area by O$_2$ plasma etching (Supporting Information). Figure 3b shows the schematic of a SWCNT network transistor. The $I$--$V$$_g$ curve of a typical transistor with a low-density SWCNT network (1 min deposition) exhibiting an on/off ratio of $10^5$ and mobility of $\sim 3\, cm^2/(V\, s)$ is shown in the inset of Figure 3b and is estimated by using a parallel plate capacitance approximation. It is worth noting that mobility analysis by this approximation can significantly underestimate the mobility in cases where the gate dielectric is thin when compared to the tube separation, and in those cases, a more detailed analysis of gate capacitance coupling should be applied. A higher-density networks (2 to 3 min deposition) exhibited mobility of over $20\, cm^2/(V\, s)$ but with reduced on/off ratios (Supporting Information, Figure S6). A semiconductor parameter analyzer (4155A, HP) was used for the electrical measurements of the SWCNT network transistors in air at room temperature. A similar dry-transfer technique was applied to the fabrication of TFTs on a flexible, transparent polymer material (inset in Figure 3a).

SWCNT networks are particularly convenient for applications in optoelectronic devices such as OLEDs. Figure 4 shows a schematic diagram of an OLED, actual light emission colors, current density versus voltage ($j$--$V$), luminance versus voltage ($L$--$V$) curves of low density, and highly transparent SWCNT sheets with different light-emitting materials. The active layers consisted of the following conjugated polymer materials: poly[9,9-diocystiylfluorene] (PFO), poly[(9,9-diocystiylfluorenyl-2,7-diyl)-co-(4,4-N(4-sec-butylphenyl))diphenylamine)] (TFB), and poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (Supporting Information). The devices showed luminance of as high as 2000 cd/m$^2$ in the case of blue-emitting polyfluorene copoly-
meres TFB and PFO. A significant advantage of the present SWCNT films deposited by the dry-transfer technique for OLEDs is that it allows the creation of very low density networks that cannot be easily made by any other technique including dry spinning from CVD forests. Importantly, MWCNT sheets are not very flexible on small scales and may act mechanically as strong needles, which can electrically short through the thin emissive layer. The low-density SWCNT network was also found to be the most appropriate for the balanced injection of holes in OLEDs. Compared to brittle ITO, the extreme flexibility and high elasticity of SWCNT films open an avenue to a fully flexible OLED.

To conclude, we have demonstrated a fast, simple dry-transfer method of preparing SWCNT network films with easily tunable optical transparency and sheet resistance on various substrates. The method avoids liquid-based dispersion and purification steps, which are needed with traditional SWCNT film production techniques. Chemically doped SWCNT networks showed sheet resistance of as low as 110 Ω/□ at T = 90%, which matches the typical ITO performance on flexible polymer substrates and to our knowledge is one of the lowest reported sheet resistances for SWCNT-based transparent electrodes. The sheet resistance of the SWCNT networks is found to be strongly dependent on the average bundle length of the produced SWCNTs. For films thicker than several monolayers, the optical transmittance and the electrical sheet resistance can be described by a simple phenomenological relation with an effective figure of merit K reflecting the properties of SWCNTs. The applicability of the dry-transfer method was demonstrated by applying it to fabricate optically transparent capacitive touch sensor electrodes, thin-film transistor channels, and OLED electrodes.

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**Supporting Information Available.** Sample preparation. Flexibility demonstration. Capacitive touch sensor demonstration. Electron and atomic force microscopy characterization of SWCNTs. Examples of SWCNT deposits on various substrates. Postdeposition treatment of SWCNTs. SWCNT thin film transistor fabrication. Fabrication of bright OLEDs with SWCNT electrodes. Uniformity of the SWCNT electrodes and sample reproducibility. This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES AND NOTES**


