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Conducting transparent thin films based on Carbon Nanotubes — Conducting Polymers
Single-walled carbon nanotube transparent conductive films fabricated by reductive dissolution and spray coating for organic photovoltaics

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Solutions of unbundled and unbroken single-walled carbon nanotubes have been prepared using a reductive dissolution process. Transparent conductive films spray-coated from these solutions show a nearly twofold improvement in the ratio of electrical conductivity to optical absorptivity versus those deposited from conventional aqueous dispersions, due to substantial de-aggregation and sizable nanotube lengths. These transparent electrodes have been utilized to fabricate P3HT:PCBM organic solar cells achieving power conversion efficiencies up to 2.3%, comparable to those of solar cells using indium tin oxide transparent electrodes. © 2014 AIP Publishing LLC.

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One of the great challenges in the field of organic electronics has been the replacement of the ubiquitous transparent electrode material, indium tin oxide (ITO), with an earth-abundant, low-cost, solution processable, and flexible alternative.1–5 Several transparent conducting films (TCFs) have emerged as potential replacements for ITO, including conducting polymers,6 silver nanowires,7 graphene,5,8 and single-walled carbon nanotubes (SWNTs). SWNTs are a promising alternative to ITO due to the great abundance of carbon; the potential for cost reduction due to economies of scale; exceptional flexibility and conductivity; and the ability to deposit nanotube networks from solution using additive, low-temperature printing and coating processes.5,8,9 Carbon nanotube TCFs have been successfully utilized in organic optoelectronic devices, including light-emitting diodes,8 photodiodes,10 and photovoltaics.12–16

However, while SWNTs have the potential to form networks with simultaneously high conductivity and high transparency, experimentally measured conductivity of transparent SWNT networks tends to be much lower than that of ITO. This is in large part because the typical ink fabrication method, dispersing SWNTs in water with the aid of sonication, damages and shortens the SWNTs.16,17 Conductivity in thin SWNT networks follows the percolation theory and is further limited by contact resistance at the tube-tube junctions. Therefore, to achieve high conductivity, a SWNT network should consist of individual tubes or small bundles, which have low contact resistance and a large number of percolation pathways, and the SWNTs should be of maximum length to minimize the number of junctions.18–20 An alternative ink fabrication method known as reductive dissolution has been developed to produce solutions of highly dispersed and unbroken SWNTs.21,22 In these processes, SWNTs are chemically reduced in the presence of an alkali metal either in liquid ammonia or in a naphthalenide solution in tetrahydrofuran. The reactive media is then removed, leaving a nanotubide salt that dissolves with only gentle mechanical stirring, without sonication, in a polar organic solvent such as dimethylsulfoxide (DMSO) or dimethylformamide. In this work, the reductive dissolution technique using liquid ammonia is employed to produce SWNT TCFs with improved conductivity versus those deposited from aqueous dispersion. We then demonstrate the use of these SWNT TCFs in organic photovoltaic (OPV) devices as the transparent anode.

CVD-grown SWNTs were purified and processed at Linde Nanomaterials. The organic SWNT ink was prepared using the liquid ammonia reductive dissolution technique developed by Fogden et al.21,22 In this process, SWNTs were chemically reduced in the presence of sodium and liquid ammonia, and the resulting nanotubide salt was dissolved in DMSO with magnetic stirring. Processing and deposition of the organic ink was performed in a glovebox; after deposition by spray coating, the films were maintained under clean dry air overnight to oxidize the nanotubide to the neutral species. An aqueous SWNT dispersion was also produced, by sonicating SWNTs in water with sodium dodecylbenzenesulfonate surfactant, and deposited under ambient conditions by spray coating. Various SWNT film thicknesses were deposited onto glass substrates, using multiple layers to produce thicker films ranging in thickness from about 20 to 100 nm. Thickness of the SWNT films was determined by scratching the films and measuring the step height with atomic force microscopy (AFM). Both aqueous and organic SWNT films were immersed in a solution of nitric acid (at least 1 M) diluted to 10% in isopropanol, to remove residual surfactant or alkali metal salt and to p-dope the nanotubes. UV-visible transmittance and Raman spectroscopy showed no significant changes after the nitric acid treatment, indicating no significant damage to the nanotubes.
To determine the FOM, the sheet resistance of the SWNT TCFs was measured using the 4-point probe technique, while the transmittance was measured by UV-visible spectroscopy. Sheet resistance and transmittance values are shown in Figure 2(a) for SWNT films of various thicknesses: the thinner the film, the more transparent. Due to the considerable SWNT length, smaller bundle size, and absence of surfactant, TCFs from the reductive process ink consistently afforded higher performance (average FOM = 15, minimum 12) than that from the aqueous dispersion (average FOM = 26, minimum 24). The performance of the aqueous SWNT film is in good agreement with that previously reported in the literature for spray-deposited aqueous dispersions,\(^\text{10}\) while the organic SWNT is competitive with some of the best performing carbon nanotube films.\(^\text{25–29}\) AFM, transmittance, and spot-to-spot Raman measurements show good uniformity and consistent results for each film. An AFM micrograph for an organic SWNT film, showing the topographical uniformity of the film, is given in Figure 2(b).

The suitability of the organic SWNT films as a transparent electrode was assessed through their integration into OPV devices. OPVs were fabricated using thin (311 \(\Omega\) \(\square\), 93% transmittance) and thick (78 \(\Omega\) \(\square\), 78% transmittance) SWNT films, and compared with control devices fabricated on ITO-coated glass slides (Thin Film Devices, 20 \(\Omega\) \(\square\), ITO film transmittance of 96.5%). To complete the solar cell structure, a 40-nm-thick hole transporting layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios P VP AI 4083, mixed with 3% DMSO and 22% isopropanol to improve its conductivity and ability to wet the SWNT film) was spin-cast onto the TCFs and baked at 130 °C for 10 min. The addition of PEDOT:PSS reduced the SWNT film sheet resistance by about 30% and the transmittance by about 4%. The active layer, a 220-nm-thick bulk heterojunction of 1:1 poly(3-hexylthiophene):[6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (P3HT:PCBM) was spin-cast from a 1,2-dichlorobenzene solution and solvent annealed at room temperature under a petri dish overnight. Aluminum cathodes were deposited by thermal evaporation, and the solar cells were annealed at 150 °C for 10 min. All active layer solution preparation and film processing were carried out in a glovebox. Each sample was patterned with several small cells (3 mm\(^2\) each) with three different distances to the anode contact, as shown in Figure 3(a), to investigate the impact of this distance on the series resistance and fill factor (FF) of the resulting devices.

Table I summarizes the performances obtained for the ITO- and SWNT-based solar cells, as measured under
TABLE I. Average solar cell performance parameters using ITO, thin SWNT, as shown in Figure 3(c). The lower transmittance of the SWNT film roughness, resulting in a lower open-circuit voltage, however, had increased leakage currents due to the higher cell performances. The devices using the thick SWNT film, electrode lies well within the typical range of the ITO solar cell performances. The devices using the thick SWNT film, however, had increased leakage currents due to the higher SWNT film roughness, resulting in a lower open-circuit voltage, as shown in Figure 3(c). The lower transmittance of the thicker SWNT film also reduced the short-circuit current density slightly.

It is important to note that the highest OPV performance with the thin SWNT film was obtained with the shortest distance to the anode contact, which is 1 mm. The disadvantage of a high transparent electrode sheet resistance such as this SWNT film is that it increases the series resistance of the solar cell, reducing the fill factor. This effect is amplified when charge carriers must travel a long distance within the transparent electrode before reaching a lower-resistance, opaque metal contact. Figures 3(d) and 3(e) show the increase in series resistance and reduction in fill factor, respectively, as the distance to the anode contact is increased. With the longest distance (7 mm), the effect of the series resistance is so severe for the solar cell with the thin SWNT film that the efficiency decreases to 2.0%, below that of the thick SWNT film. Cells with the lower-resistance TCFs (thick SWNT and ITO), on the other hand, have lower series resistance and a less significant reduction in FF for the longer distances.

For applications in large area modules, OPV devices should have higher overall efficiencies and larger active area than those presented in this work. Higher efficiencies can be achieved through the use of optimized processing conditions for the P3HT:PCBM, a lower-bandgap polymer in place of the P3HT (see, e.g., Pierre et al. 30), or a lower work function cathode material. To achieve larger active areas while minimizing losses due to series resistance, it will be necessary to add a metal grid to the SWNT film, as has been proposed in the past to supplement SWNT. 15,31 PEDOT:PSS,6 and ITO32 TCFs. This requirement will become even more stringent if a lower-bandgap polymer is used in the active layer, as the increase in photocurrent density would increase the resistive losses. Nevertheless, the enhancement in TCF conductivity achieved with the reductive dissolution process represents an important step toward the viability of SWNT films as an ITO replacement for organic optoelectronics. We expect these SWNT films to become increasingly competitive with further optimization of the processing and deposition techniques, particularly on flexible plastic substrates, and as the continued scaling up of SWNT production lowers the manufacturing costs.

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