DOI: 10.1002/ejic.201100396

Low-Cost and Ultra-Strong p-Type Doping of Carbon Nanotube Films by a Piranha Mixture

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Keywords: Nanotubes / Conducting materials / Doping / Piranha mixture / Carbon

Recent studies have demonstrated that single-walled carbon nanotube (SWCNT) films can be doped by a nitric/sulfuric acid treatment to significantly improve its conductivity. However, the sheet resistance is still too high for many applications. Here we report on a simple treatment using a piranha mixture that could further enhance SWCNT film conductivity. The high redox potentials of hydrogen peroxides combined with the acidity of sulfuric acid enabled strong p-doping of the carbon nanotube films. Absorption peak suppression and a G-band shift provided proof of strong p-doping of the SWCNT films.

Introduction

Indium tin oxide (ITO), as a transparent conductor, has been widely used in many different electronic devices such as LCD/LED displays, touch screens, and organic solar cells.[1] However, because of its chemical instability, poor flexibility, high-cost of fabrication, and limited indium source, much research has been conducted to find alternatives.[2–6] Among all the candidates, single-walled carbon nanotube (SWCNT) based transparent thin films have been demonstrated to possess very low sheet resistance (R_s).[7]

The as-prepared SWCNT electrodes have to be treated with gold trichloride ($AuCl_3$),[6,7] nitric acid (HNO_3),[8] thionyl chloride ($SOCl_2$),[9] sulfuric acid (H_2SO_4),[10] or a halogenated compound[11,12] in order to improve their electrical properties. The enhancement of electrical conductivity has been attributed to (1) the removal of surfactants that are present in carbon nanotube films;[4] or (2) the attachment of a –COCl group that could enable p-doping into the carbon nanotube with electron withdrawal;[9,13] or (3) the formation of COOH and SO_3H, which are beneficial for conductivity enhancement;[14,15] or (4) element doping to perform Fermi-level engineering of nanotubes and to attain very high conductivity.[2,16]

Nevertheless, on the basis of current approaches, highly conductive carbon nanotube films can only be obtained by using self-grown carbon nanotube products, delicate separation/purification processes,[16] or high-cost chemical doping agents.[6,7] Such disadvantages have encouraged us to develop a simple and inexpensive method to improve the conductivity of carbon nanotube films.

Here we demonstrate that commercially available carbon nanotube based (P2 and P3 from Carbon Solution Inc. and CG200 from Southwest Nanotechnologies) films can achieve high conductivity (ca. 150 ohm/sq with 85% transmittance) through the treatment of a commonly used agent, a piranha solution (a 3:1 mixture of sulfuric acid and hydrogen peroxide).

Results and Discussion

Optical absorption spectra of the films prepared from pristine CNTs are shown in Figure 1. The peak E11 for P2

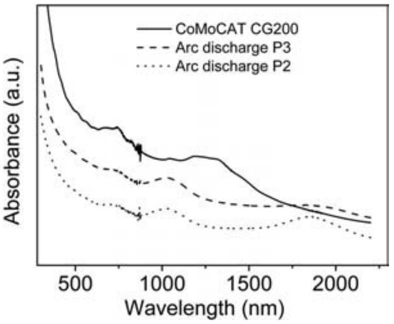

Figure 1. UV/Vis absorption of different SWCNT films.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100396.

and P3 arising from the first Van Hove singularity is at 1800 nm, whereas the E11 peak for CG200 is at around 1300 nm. The position difference of E11 is due to the larger diameters of P2 and P3 CNTs.[17] Interestingly, the E11 absorption peak for P3 is not as strong as that for P2, and it has been reported that P3 CNTs show up-shifted Raman spectra compared to P2.[15] Such suppression and up-shifted Raman spectra are possibly from the self-p-doping by its –COOH functional group.[15] This kind of p-doping could enhance its conductivity, and our results (Figure 2) prove that the pristine P3-based film has a higher conductivity than the P2 film.

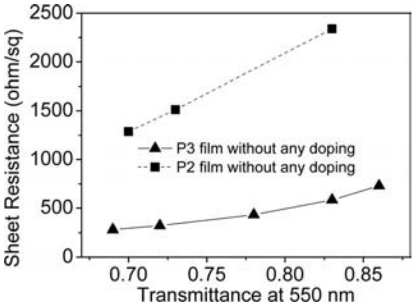

Figure 2. Sheet resistance of pristine P2 and P3 films.

Figure 3 shows the sheet resistance of different SWCNT films after sulfuric acid treatment. The P3 film, prepared with 0.5 wt.-% SDBS, shows a significantly better conductivity compared with that of the P3 film, prepared from a solution without SDBS. The AFM characterization in Figure 4 shows that the SDBS surfactant could help the carbon nanotube to attain a favorable morphology for better conductivity.[5] Figure 4(a) (P3 film without SDBS) shows an uneven distribution of CNT density. In some areas the aggregated islands of CNTs can clearly be observed. In comparison, Figure 4(b) (P3 film with SDBS) shows a more even distribution of carbon nanotube density across the space. Figure 4(c) (CG200 with SDBS) shows that CG200 is evenly distributed and a smoother film. Even though CG200 shows the best morphology among all the films (less particles and impurities), its conductivity is not as high as that of the P2 and P3 CNT films. Therefore, we believe that the CNT diameter might be a more important parameter, although the morphology does play a role in attaining a high-conductivity film. Namely, a large-diameter carbon nanotube exhibits a lower band-gap energy and higher carrier concentration that could improve the overall film conductivity. The air-spray deposition method may not be the best method to achieve uniform-morphology films. In fact, vacuum filtration, rod-casting, or the layer-by-layer (LBL) method[5] could fabricate a much smoother morphology, but air-spray deposition is definitely the fastest method to deposit carbon nanotube films. One film of carbon nano-

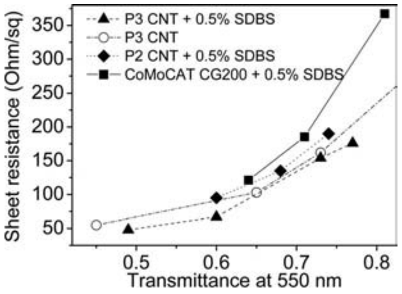

Figure 3. Sheet resistance of SWCNT films prepared from different solution formulations.

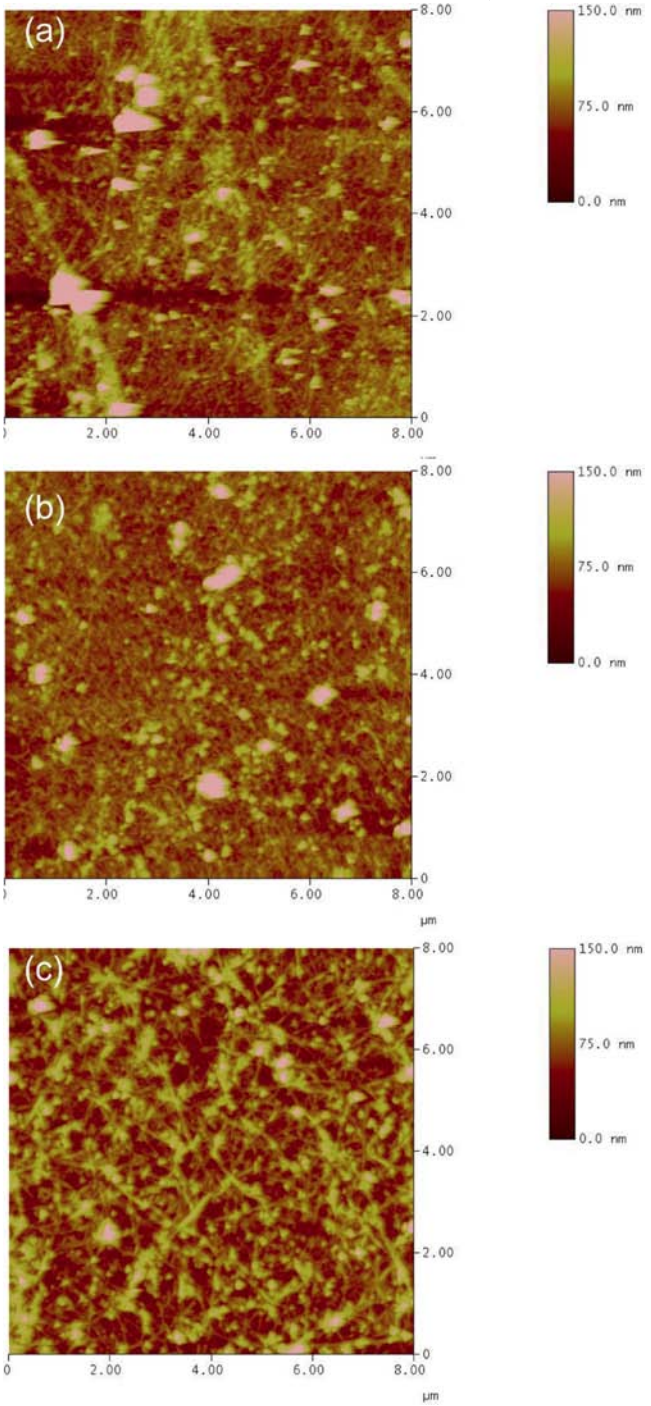

Figure 4. AFM image of different carbon nanotube films prepared from (a) P3 solution without SDBS, (b) P3 solution with 0.5 wt.-% SDBS, and (c) CG200 with 0.5 wt.-% SDBS.

tube film can be fabricated in less than 5 min by air spray, whereas it would need 1–2 h to fabricate one film by the vacuum-filtration method.

Figure 5 shows the effect of sulfuric acid treatment on P3-CNT-based films. The CNT films are doped step-by-step by sulfuric acid until most of the absorption peaks are suppressed.[18] Generally, the film was immersed in an acid solution for 15 min and washed with water before testing. From Figure 5(a) it is concluded that the conductivity of CNT-based films increases with increasing acid concentration from 20 to 70%. When the acid concentration is higher than 70%, the absorption and conductivity show no obvious changes, which means that the acid doping has reached a limit. Acid treatment is one simple way to improve carbon nanotube film conductivity, with limited doping power, as can be observed in Figure 5.

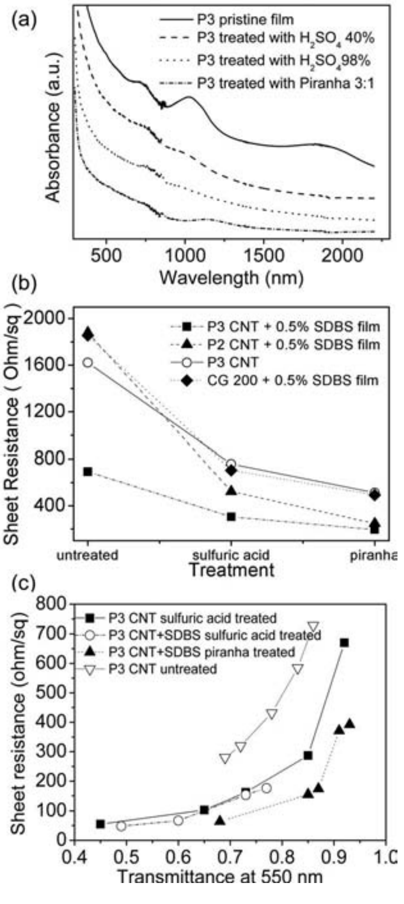

Figure 5. UV/Vis spectra (a) and Sheet resistance (b) change with increasing acid concentration treatment.

Since the conductivity of the above-mentioned CNT film is still insufficient as an indium tin oxide replacement (sheet resistance is still in the range of ca. 280 ohm/sq with 85% transmittance) a new dopant agent, which has a very high reduction potential (strong oxidant), is needed to withdraw even more electrons from the carbon nanotube. Hydrogen peroxide is used as one of the candidates. Hydrogen peroxide shows a high redox potential, E^0 of 1.78 V.[19] Because H_2O_2 needs acidic conditions to enhance its reaction, a mixture of H_2O_2 and H_2SO_4 (piranha mixture, consisting of a 3:1 mixture of sulfuric acid and hydrogen peroxide) was used. With the piranha mixture, the conductivity of the P2, P3, and CG200 CNT-based films could be lowered even further. The best result was achieved with the P3 + 0.5% SDBS film, where the sheet resistance could be lowered from ca. 280 ohm/sq with 85% transmittance to ca. 150 ohm/sq with 85% transmittance as shown in Figure 6(b). The UV/Vis spectroscopy measurements in Figure 6(a) show a further suppression of most of the carbon nanotube peaks, especially the S22 peaks; we observed a significant dip in the absorption peaks. The piranha mixture could possibly contribute to the removal of SDBS surfactants; however, the morphology of the CNT films observed by AFM has shown no changes (see Supporting Information). This means that the conductivity enhancement by the piranha mixture purely arises from the enhanced p-doping. The p-doping could affect all types of CNTs; the large-diameter P2 and P3 and the smaller-diameter CG200 CNTs. However, because of the superior inherent conductivity of the P2 and P3 CNTs, the doped conductivity of P2 and P3 is better than that of the CG200 CNT.

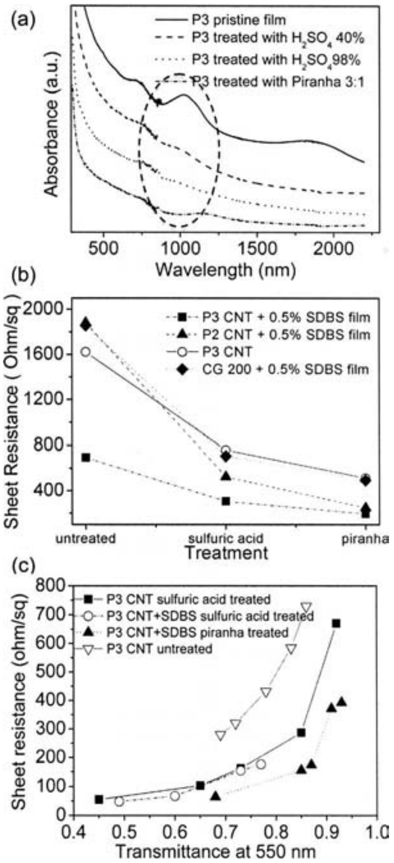

Figure 6. Effect of the piranha mixture doping on (a) the UV/Vis spectra, (b) the sheet resistance, and (c) the sheet resistance/transmittance curve of carbon nanotube films.

This highly conductive CNT film is stable for weeks in an ambient environment. Raman spectroscopy performed on the P3 carbon nanotube film, shown in Figure 7, indicates that the G-band frequency shifts to a higher wavelength, suggesting the occurrence of p-doping in the carbon nanotubes.[7] The wavenumber shift of the G-band by the piranha mixture doping was larger than that for normal acid treatment, which further proves that the piranha mixture has a stronger p-doping effect compared with normal acid. Previous studies have shown a similar phenomenon by using $AuCl_3$ at high concentration.[6,7] However, even though $AuCl_3$ is a strong p-dopant, it is a high-cost chemical, which is economically not viable for large-scale production.

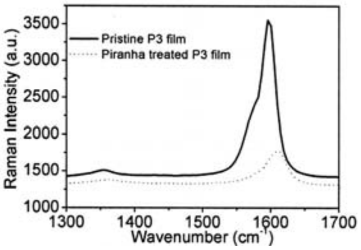

Figure 7. Effect of piranha doping on the Raman spectra.

Even though this value of ca. 150 ohm/sq with 85% transmittance at 550 nm has been observed in other reports,[7–9] the main point highlighted here is that we are using commercially available carbon nanotubes without further purification or separation and an inexpensive chemical agent as the dopant. The key to achieving highly conductive carbon nanotube films while maintaining its scalability is through introducing stronger doping agents that could enhance the carbon nanotube carrier concentration. The mixture of sulfuric acid and hydrogen peroxide has been shown to be a good choice as the dopant because of its high reduction potential. With its high reduction potential it is able to inject more protons into the carbon nanotube, which we observed with the further suppression of the absorption peak and enhanced G-band shift in the Raman spectra.

Conclusions

In this research, a piranha solution has been demonstrated as a cheap and better dopant to achieve highly conductive CNT films from commercially available CNTs (i.e. carbon nanotube from Carbon Solution Inc.) and not from specially produced carbon nanotubes. The doping mechanism of the piranha solution is similar to the acid doping. The only difference is that hydrogen peroxide has a higher oxidation potential and so has a stronger tendency to withdraw electrons from CNTs than normal acids. Our procedure has been proved to be repeatable and scalable. More importantly, our process does not involve any filtration or separation steps, which is a time-consuming process and may cause loss of CNTs. Our procedure has demonstrated that 1 mg of carbon nanotube could produce five pieces of 1 inch × 1 inch CNT films in less than 20 min.

Experimental Section

The arc-discharge P2 and P3 CNTs were purchased from Carbon Solution Inc., and the CVD-produced CNTs (denoted as CG200) were bought from Southwest Nanotechnologies. All CNTs were used as received without further purification. The P2 CNT is a non-functionalized carbon nanotube, and P3 is a COOH-functionalized CNT. The P2 and P3 CNTs have relatively larger diameters than the CG200 CNTs. To prepare homogeneous CNT films, CNT (4 mg) was added to water (20 mL) containing sodium dodecylbenzenesulfonate (SDBS) surfactant (0.5 wt.-%), followed by 30 min of probe sonication (Sonics Vibra Cell, 20 Hz, 120 W). The resulting solution was centrifuged at 6000 rcf for 30 min. The thin-film fabrication was carried out by air spraying onto a glass substrate. The as-prepared film was soaked in water to remove the majority of the surfactants. Note that the P3 carbon nanotube could be dissolved in water without the addition of any surfactant; however, the use of surfactants does help to enhance its morphology[5] and in turn results in better conductivity. The conductivity measurements were performed with a 4-point probe system (Signatone). The optical transmittance of the CNT thin film was measured with a UV/Vis spectrometer (Perkin–Elmer Lambda 900), and the morphology was explored by Atomic Force Microscopy (AFM, Digital Instruments).

Supporting Information (see footnote on the first page of this article): AFM section analysis of the CNT conductive films.

Acknowledgments

Q. Z. acknowledges the financial support from the Nanyang Technological University (start-up grant) and the AcRF Tier 1 (RG18/09) from the Ministry of Education, Singapore. L. J. L. acknowledges the support from Academia Sinica, National Science Council Taiwan (NSC-99-2112-M-001-021-MY3 and 99-2738-M-001-001) and the National Research Foundation, Singapore (NRF-CRP2-2007-02).

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Received: April 12, 2011