Dispersion of single-walled carbon nanotubes by DNA for preparing transparent conductive films†

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Single-walled carbon nanotubes dispersed by pristine DNA and denatured DNA were used to prepare transparent conductive films on PET substrates by a vacuum filtration and spray coating method. Transmission electron microscopy (TEM) was used to characterize the dispersion state of SWCNT solutions. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used to investigate the interaction between SWCNTs and DNA. It was found that both pristine and denatured DNA could effectively disperse SWCNTs. Acid treatment on SWCNT films degraded and removed DNA molecules effectively. The sheet resistance of SWCNT-DNA films was reduced by a factor of 2.5–10 times after acid treatment while the change of transmittance was negligible over the visible region. Films with high performance (95 Ω/sq, 78%) and good stability have been obtained.

Introduction

Transparent conductive carbon nanotube films have gained great interest of world wide researchers in recent years due to their good durability and flexibility, ease of processing, low reflectance, and natural color. These advantages allow CNT films to be widely used in electronic devices such as touch screens, liquid crystal displays (LCDs), organic light-emitting diodes (OLEDs) and photovoltaics[1–4] and to be a candidate for replacing ITO. A lot of methods have been used to fabricate carbon nanotube films including air brushing,[1] drop casting from solvents,[5] spin coating,[6] dip casting,[7] Langmuir–Blodgett deposition,[8] vacuum filtration,[9] and spray coating.[10] Among these methods, vacuum filtration and spray coating are the most efficient and commonly used ones due to their simple process, good film homogeneity and controllability of film thickness.

Before films are made, a crucial step is to obtain homogeneous and stable carbon nanotube solutions with a small bundle size. However, most commercial SWCNTs are aggregated due to strong van der Waals forces between them. Several strategies have been developed to debundle SWCNTs including covalent modification and noncovalent modification. Covalent modification will induce some defects on the side walls and decrease the conductance of SWCNTs.[11] In contrast, noncovalent wrapping is the most efficient route to obtain debundled SWCNT solutions with less damage. Commonly used dispersants are surfactants, polymers and biomolecules. Unfortunately, most of them are nonconductive and their remnants in the films will increase the sheet resistance. Therefore, conductive or easily removable dispersants are expected to improve the performance of SWCNT films. Conductive polymers such as poly (3,4-ethylenedioxythiophene)/poly styrenesulfonate (PEDOT/PSS),[12] polyaniline boronic acid (PABA),[13] poly-3-alkylthiophenes (P3AT)[14] and polyaniline (PANI)[15] have been used to decrease the sheet resistance of SWCNT films. However, these conductive polymers are colored and adsorb light over the visible region, which will decrease the transmittance of CNT films. Therefore, dispersants with the following characteristics are preferable. (1) They can disperse SWCNTs into small bundles or even into individual ones. (2) They are easily removed. (3) They have no absorption over the visible region.

DNA is a natural macromolecule which plays an important role in combining the materials and biology area.[16] There are two kinds of unique bonds in DNA molecules, the glycosidic bond and the phosphodiester bond. Phosphodiester bonds connect pentoses to form the backbones of DNA, while glycosidic bonds connect the bases with the backbones. Generally, there are four kinds of bases in DNA, adenine (A), guanine (G), thymine (T) and cytosine (C). They all contain a basic six-membered ring composed of carbon and nitrogen. In a physiological environment, DNA keeps a stable double helix structure due to hydrogen bonds between the two single strands. They will turn into single strands when heated and the absorption at 260 nm will increase.[17] DNA has a lot of advantages which make it a good dispersant for preparing transparent conductive SWCNT films of high performance. First, they can coat, separate, and solubilize CNTs effectively with its phosphate backbone interacting with water and many bases binding to CNTs.[18] Second, as a biomolecule, DNA can be easily degraded and removed by acid or DNase. Third, DNA has little absorption over the visible range. A lot of work[19–22] reported the high efficiency of DNA to disperse SWCNTs. Helical wrapping model[20,23] has been proposed to describe the structure of DNA wrapped CNTs. The helical structure and stability of DNA on the tubes were influenced by the chemical and physical characteristics of CNTs and the ionic strength[24] of the solution. Some calculations[25] and experiments[26] indicated that in addition to π–π interactions between SWCNTs and bases of DNA, hydrogen bonds also formed. Charge transfer from the bases of DNA to CNTs has

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been calculated by Gowtham *et al.*[27] They pointed out that the interaction strength between diverse bases and CNTs was significantly different and followed the order G > A > T > C. Therefore, the DNA sequence could be optimized to improve the dispersion of SWCNTs. In addition, wrapping SWCNTs with DNA allowed the chromatographical separation of CNTs with different types and diameters according to their different electrical characteristics.[23] SWCNTs with higher content of metallic tubes could be obtained after separation by choosing an appropriate DNA sequence.

Although there are some reports on the dispersion of CNTs by DNA, little work has been done on the preparation of SWCNT transparent conductive films using DNA as the dispersant. Besides, most of the DNA used in previous work was single strand (ss-DNA). Double strand DNA (ds-DNA) was seldom used or was even predicted to be inefficient to disperse CNTs.[28] However, we found that ds-DNA was more efficient to disperse SWCNTs under certain circumstances. In our work, both pristine DNA (double-strand) and denatured DNA (single-strand) were used to disperse SWCNTs. Transparent conductive films were prepared using SWCNT-pristine/denatured DNA solutions. Nitric acid was used to degrade and remove DNA molecules to decrease the sheet resistance of the films. The removal mechanism of DNA was discussed in detail. Films with high performance (95 Ω/sq, 78%) and good stability have been obtained after acid treatment. Transparent films with such low sheet resistance are close to the criteria of flat panel displays (FPD) and have great potential applications.

Experimental methods

Chemicals

The P3 SWCNTs purchased from Carbon Solutions Inc. were synthesized by the arc-discharge method and were purified with nitric acid as claimed by the provider. This kind of nanotube contains 1.5–3.0 atomic% carboxyl groups. DNA (double-strand, salmon sperm, 2000 base pairs) was obtained from Sigma Chemicals.

Dispersion of SWCNTs

DNA was dissolved in water using two different methods. In one way, 10 mg pristine DNA was added into 50 mL deionized water and was stirred at room temperature until it was dissolved. Pristine DNA solution was obtained in this way. In the other way, 10 mg pristine DNA was added into 50 mL deionized water followed by boiling for 10 min. The solution was rapidly cooled down to room temperature in ice water and denatured DNA solution was obtained. 10 mg P3 SWCNTs were horn sonicated in 50 mL of the above DNA solution and were centrifuged at 13 000 rpm for 30 min. The supernatant was carefully collected and subjected to another round of 30 min centrifugation at 13 000 rpm.

Film fabrication

1. SWCNT films were prepared by vacuum filtration method. The supernatant was diluted 10-fold with water. Then 10–60 mL solutions were filtrated through a 220 nm Millipore ester membranes to prepare films. After filtration, the membranes were then transferred onto PET substrates, dried in air at 90 °C for 1 h and then dipped in acetone for 30 min to dissolve the membrane. The obtained films were dried at 90 °C for 2 h and were further immersed in 14 M nitric acid for a certain time and rinsed with abundant deionized water. After drying at 60 °C for 12 h, the sheet resistance of the films was measured.

2. SWCNT films were prepared by spray coating method. The instrument was assembled by ourselves and its sketch map is shown in Fig. S1 in the ESI.† 1–5 mL of the above denatured DNA dispersed SWCNT solution was added into a spray gun which was connected with an argon cylinder. PET substrates were placed on a electric hot plate and preheated to 120 °C. Then, SWCNT solutions were sprayed onto the PET substrate with argon as the carrier gas at a flow rate of 2 L min^{-1}. After that, the films were subjected to acid treatment with 14 M and 5 M nitric acid, respectively, and rinsed with abundant deionized water. They were kept drying at 60 °C for 12 h, the sheet resistance of the films was measured.

3. SWCNT reference films were prepared by spray coating method. The procedure to prepare SWCNT solutions and the films is the same as the above process except that no DNA was added.

Characterization

The dispersion states of SWCNTs were characterized by TEM (JEM-2100F, JEOL, Tokyo, Japan). SEM images of SWCNT films were taken on a field emission scanning electron microscope (FESEM, JEOL, JSM-6700F). The transmittance of films at 550 nm was measured *via* a UV-vis spectrometer (Lambda 950, Perkin-Elmer, Shelton, USA). A four-point probe resistivity meter (Loresta EP MCP-T360, Mitsubishi Chemical, Japan) was used to measure the sheet resistance of the films. X-ray photoelectron (XPS) analysis was conducted using the Mg-Kα (1253.6 eV) monochromatic X-ray source (Axis Ultra DLD, Kratos). Raman spectra were recorded on a Renishaw Micro-Raman spectrometer with an excitation length of 633 nm.

Results and discussion

Dispersion of SWCNTs

The dispersion state of SWCNTs in DNA solutions was characterized by TEM. In Fig. 1a, DNA was denatured by boiling for 10 min followed by cooling down to room temperature rapidly and then was used to disperse SWCNTs. In this case, most of the DNA molecules have been turned into single-stranded since their absorption at 260 nm increased from 0.33 to 0.52 (ESI† Fig. S2). In the case of Fig. 1c, DNA was dissolved at room temperature and most of the DNA molecules were kept double-stranded. From Fig. 1a and 1c, we can see that the bundle size of SWCNTs dispersed by both pristine and denatured DNA was small and homogeneous, which indicated higher dispersion ability of DNA than other dispersants used in our previous work, including SDBS, SDS, Nafion[9] and P123.[29] Bundle size distributions measured from the corresponding TEM images were shown in Fig. 1e and 1f. The bundle size of SWCNTs dispersed by denatured DNA was about 2–6 nm, while that of SWCNTs dispersed by pristine DNA was somewhat thinner, about 3 nm. The helical

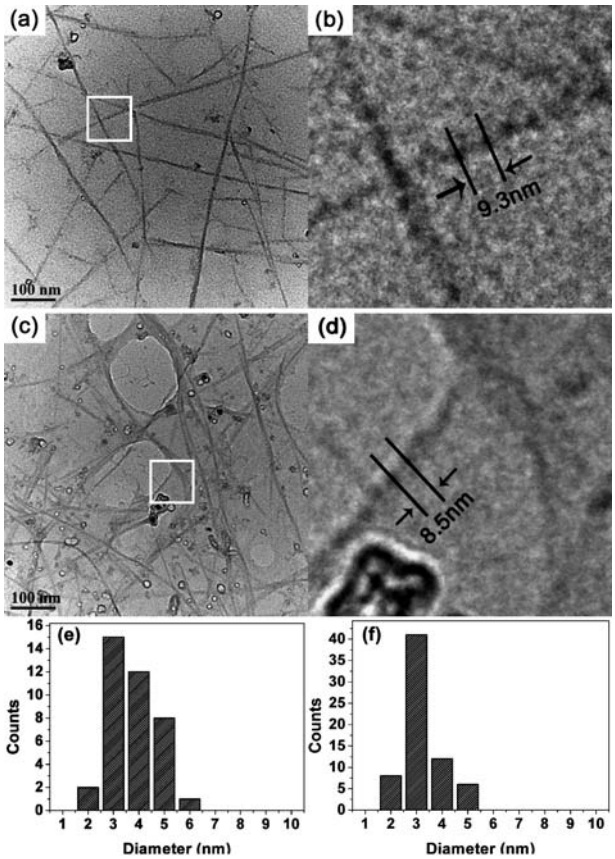

Fig. 1 TEM images and the corresponding bundle diameter distributions of SWCNT solutions dispersed by denatured DNA (a), (e) and pristine DNA (c), (f); (b) magnified image of the labeled part in (a); (d) magnified image of the labeled part in (c).

structure of DNA wrapped SWCNT with helical pitch about 8–10 nm can be observed from Fig. 1b and 1d. The concentration of both the as-prepared suspensions was 0.2 mg mL^{-1}. After centrifugation, some thick bundles were discarded and the absorbance decreased. The concentration after centrifugation was calculated according to the equation $X_F = X_I{*}A_F/A_I$, where X_I/X_F is the concentration before/after centrifugation and A_I/A_F is the absorption at 500 nm before/after centrifugation. The concentrations of SWCNT solutions dispersed by pristine and denatured DNA were about 0.187 mg mL^{-1} and 0.124 mg mL^{-1} after centrifugation. They stayed stable for at least 3 months with no visible sedimentation.

Although Enyashin *et al.*[28] and Zheng *et al.*[21] reported that single-strand DNA (ss-DNA) was more effective to disperse SWCNTs, our results showed that double-stand DNA (ds-DNA) was better to disperse P3 SWNTs. In Zheng's work, 0.1 M NaCl and pH buffer solution was added to keep the helix structure of DNA.[19] In our case, no additional salt was added since it might affect the performance of the films. In order to investigate the influence of ionic strength on the dispersion ability of DNA, DNA solutions with 0.1 or 1 M NaCl were prepared and used to disperse SWCNTs. Seen from Fig. 2, the absorption intensity of SWCNT solutions decreased obviously with the increase of the ionic strength, which indicated the concentration of SWCNTs decreased. This can be rationalized when we consider that Na^+

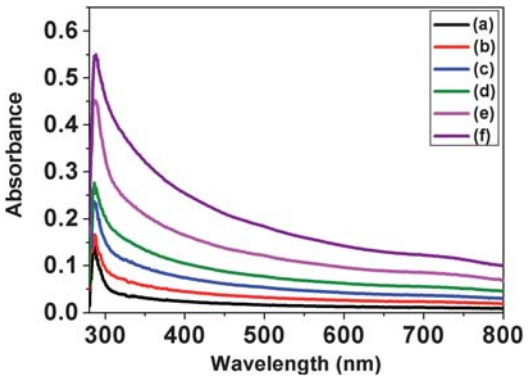

Fig. 2 Absorption spectra of SWCNT suspensions dispersed by (a) denatured DNA in 1 M NaCl; (b) pristine DNA in 1 M NaCl; (c) denatured DNA in 0.1 M NaCl; (d) pristine DNA in 0.1 M NaCl; (e) denatured DNA; (f) pristine DNA.

can neutralize the negative charges of $–COO^-$ and PO_4^- on the surface of SWCNTs and lower the electrostatic repulsive force between them. The absorption intensity of SWCNT-denatured DNA solution was always lower than that of SWCNT-pristine DNA solution in the presence of salt. This again proved the better dispersion ability of ds-DNA. The deviation between Zheng's findings and our results might be because we used different SWNTs and DNA molecules, since physicochemical and electronic properties of nanotubes would influence their interaction with DNA. From the perspective of both dispersion and film fabrication, pristine DNA is the preferred dispersant.

Investigation of the performance of SWCNT-DNA films

SWCNT solutions dispersed by pristine and denatured DNA were used to prepare films using the vacuum filtration method. Films were then treated with 14 M nitric acid for an hour. The performance of the films was shown in Fig. 3a. Before acid treatment, the sheet resistance of SWCNT-pristine DNA films was lower than that of SWCNT-denatured DNA films at high transmittance (above 90%). This was mainly attributed to the better dispersion state of SWCNT solutions dispersed by pristine DNA. As the transmittance decreased, which meant the thickness of the film increased, it became more difficult for excess DNA molecules to pass through filtration membranes, especially for ds-DNA because of its larger volume. The residue of DNA played a negative role on the sheet resistance. Therefore, the sheet resistance of SWCNT-pristine DNA films get similar or even higher than that of SWCNT-denatured DNA films. After acid treatment, the sheet resistance of both kinds of films decreased considerably, by a factor of about 3–8 times with negligible change of transmittance over the visible range (Fig. 3b). The sheet resistance of SWCNT-denatured DNA films decreased more compared to that of SWCNT-pristine DNA films, because the denatured DNA molecules were more easily removed. Film with the sheet resistance of 95 Ω/sq at the transmittance of 78% was obtained after acid treatment. The influence of acid treatment time on the performance of the films was shown in Fig. 3c. The sheet resistance of SWCNT-denatured DNA film decreased significantly in the first hour and no obvious change occurred until 4 h. The sheet resistance increased slightly when

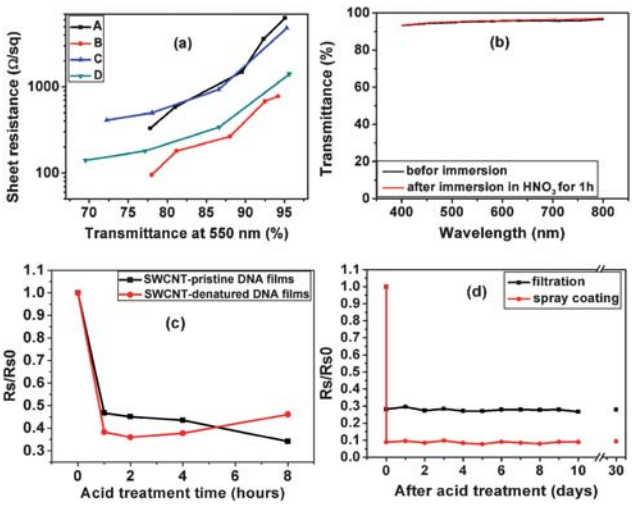

Fig. 3 (a) The sheet resistance of different SWCNT films as a function of transmittance at 550 nm, A: SWCNT-denatured DNA films; B: 14 M nitric acid treatment of A for 1 h; C: SWCNT-pristine DNA films; D: 14 M nitric acid treatment of C for 1 h. (b) The change of the transmittance before and after nitric acid treatment. (c) The sheet resistance change of SWCNT-DNA films prepared by filtration method with nitric acid treatment time. The sheet resistance was normalized by the initial sheet resistance. (d) Stability of SWCNT-denatured DNA films prepared by filtration and spray coating method after 14 M nitric acid treatment for 1 h.

the acid treatment time prolonged to 8 h. For SWCNT-pristine DNA film, the sheet resistance decreased with acid treatment time until 8 h. This again proved that pristine DNA molecules were more difficult to be removed. Therefore, from the perspective of dispersants removal, denatured DNA was preferred since PET substrate will turn brittle after a long time acid treatment. Nitric acid of low concentration ($\sim$ 5 M) was also effective to remove DNA. However, it took a longer time to degrade DNA when the concentration of H^+ was low. The sheet resistance decreased from 7000 Ω/sq to 1600–1800 Ω/sq after treatment for 24 h in 5 M HNO_3.

The sheet resistance of SWCNT-DNA films prepared by spray coating method was much higher than that of films prepared by filtration. For example, at the transmittance of 85%, the sheet resistance of SWCNT-denatured DNA films prepared by spray coating method was about 20 kΩ/sq and that of films prepared by filtration was only 890 Ω/sq. It is understandable that more DNA molecules retained in the film increased the sheet resistance greatly. After acid treatment, the sheet resistance decreased significantly, by a factor of about 10 times. Films after acid treatment showed good stability over one month as shown in Fig. 3d.

An interesting and meaningful phenomenon is that the sheet resistance of SWCNT-denatured DNA films without acid treatment decreased after being placed in the air for a couple of days. For example, the sheet resistance decreased from 400 Ω/sq to 232.4 Ω/sq after two weeks. This might owe to the degradation of denatured DNA by microorganisms in the warm and humid air.[30] No similar phenomenon was observed for SWCNT-pristine DNA films, which might be due to the difficulty in removing pristine DNA. This provides an inspiration for some effective, non-destructive and environmentally friendly routes to remove dispersants and enhance the conductivity of SWCNT films.

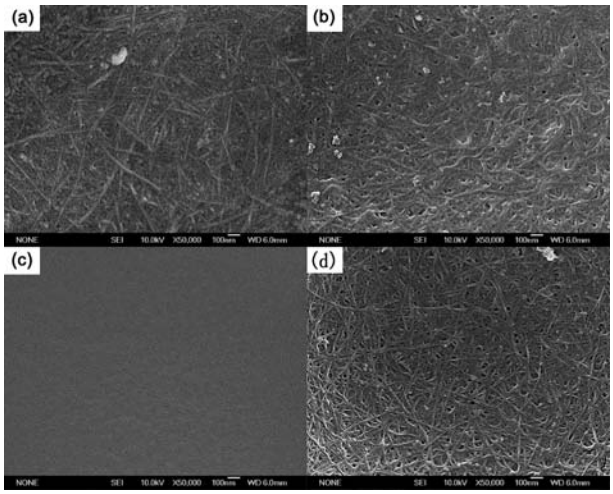

Fig. 4 SEM images of SWCNT-denatured DNA films, (a) made by vacuum filtration method; (b) 14 M nitric acid treatment for 1 h of (a); (c) made by spray coating method; (d) 14 M nitric acid treatment for 8 h of (c).

The morphology evolution of SWCNT films before and after acid treatment was shown in Fig. 4. Fig. 4a and b disclosed that after acid treatment, DNA molecules and some of the impurities were removed and the films became more dense, which was consistent with previous reports.[10] SWCNTs could not be observed in the film prepared by spray coating method because the surface was covered by DNA molecules (Fig. 4c). After acid treatment, SWCNT networks clearly appeared due to the removal of DNA molecules (Fig. 4d). The elimination of insulating dispersants and impurities together with the film densification enhanced the conductivity of SWCNT TCFs.

Conduction mechanism analysis by XPS and Raman spectra

XPS spectra were used to characterize the removal of DNA and the interaction between SWCNTs and DNA. From Fig. 5, we can see that the position of the C1s peak and the intensity of the N1s and P2p peaks changed a lot after acid treatment. The semi-quantitative analysis data obtained from the XPS spectra are summarized in Table 1. Phosphorus from the phosphodiester bond represented the existence of DNA backbones. For SWCNT-denatured DNA films, most of the DNA molecules were removed after acid treatment since no phosphorus could be detected. The intensity of the N1s peak at $\sim$401 cm^{-1} which represented C–N/N–H groups also decreased a lot after acid treatment. This again proved the removal of DNA molecules. However, the signal of this peak can still be detected due to the residual bases on the walls which will be discussed later. Broad bands at 286–290 eV which were identified as sp^3 carbon corresponded to –COOH and C–O groups.[31] Their evolution also testified to the removal of DNA molecules through acid treatment. The peak of COO^- was observed in the reference film since P3 SWCNTs had been purified with nitric acid and some carboxyl groups were induced. When DNA was introduced, the intensity of the COO^- peak decreased a lot while that of the C–O peak appeared. This was because SWCNTs were covered by DNA and the detectable depth of XPS was only 3–5 nm. The

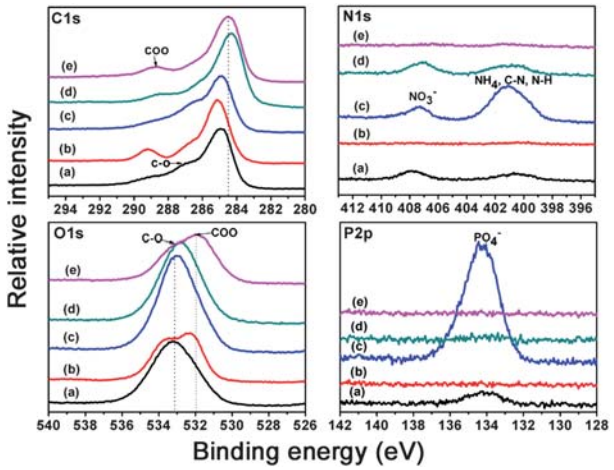

Fig. 5 XPS analysis of SWCNT-DNA films before and after acid treatment. Spectra (a) SWCNT-denatured DNA films prepared by filtration method; (b) 14 M nitric acid treatment for 1 h of (a); (c) SWCNT-denatured DNA films prepared by spray coating method; (d) 14 M nitric acid treatment for 8 h of (c); (e) reference film.

Table 1 Atomic concentration (at. %) analysis of SWCNT-denatured DNA films by XPS

Semi-quantitative analysis	C	N(NO_3)	N(C–N, N–H)	O	P
Films made by filtration method	70.0	0.5	0.4	27.2	0.2
14 M HNO_3 treatment for 1 h	75.4	0.0	0.1	22.2	0.0
Films made by spray coating method	59.6	0.4	3.0	30.6	2.0
14 M HNO_3 treatment for 8 h	69.7	0.6	0.7	25.8	0.0

intensity of the COO^- peak recovered after acid treatment indicating the removal of DNA.

The shifts of peak position were used to characterize charge transfer between DNA and SWCNTs. SWCNT films prepared without any dispersants were used as the reference film to evaluate the shift change. The main peak of C1s of the reference film appeared at 284.5 eV, which was identified as sp^2 carbon. Table 2 showed the C1s shift of different films. The main C1s peak of SWCNT-DNA film was up-shifted compared to reference film indicating the electron transfer from DNA to SWCNTs.[27,28] For SWCNT-denatured DNA films prepared by filtration method, the main C1s peak was up-shifted by 0.45 eV. More DNA molecules in SWCNT-denatured DNA films prepared by spray coating method resulted in a stronger electron donor effect and further up-shift of the peak position.

Table 2 Comparison of the XPS C1s shift

Samples	XPS C1s shift/eV
Reference films	
SWCNT-DNA films made by filtration method	+0.45
14 M HNO_3 treatment for 1 h	+0.63
SWCNT-DNA films made by spray coating method	+0.51
14 M HNO_3 treatment for 8 h	−0.19

After 1 h acid treatment, the C1s peak up-shifted further. Two points could be obtained from this phenomenon. First, there was no obvious p-doping effect after one hour acid treatment. As electron acceptor, treatment by HNO_3 was reported to p-dope SWCNT and cause the down-shift of C1s peak.[32] However, the C1s peak of the film did not down-shift after 1 h acid treatment. This indicated that no obvious p-doping effect occurred and the enhancement of conductivity was mainly attributed to the removal of DNA molecules. The control experiment was also designed to support this viewpoint. SWCNT film without any dispersant (reference film) was immersed in 14 M HNO_3 for an hour and then was rinsed with abundant water and dried at 60 °C for 12 h. The sheet resistance was measured before and after acid treatment. No obvious difference existed between the values measured before (964 Ω/sq) and after (937 Ω/sq) acid treatment. This also indicated that p-doping did not happen. Second, some bases still resided on the wall of nanotubes and donored electrons to the tubes. The residue of –NH groups in the films after acid treatment proved this point. The removal mechanism of DNA in acid solution (shown in Fig. 6) could be concluded according to these findings. Both glycosidic bond and phosphodiester bond could be hydrolyzed by acid. In the acid treatment process, the backbones of DNA molecules were separated from the bases due to the hydrolysis of glycosidic bonds and were cut into short chains due to the hydrolysis of phosphodiester bonds. These shortened apurinic residues were easily removed from the walls of SWCNTs because the connections between them were cut. However, some bases still resided on the walls due to π–π interaction between the C=N/C=C double bonds of DNA and SWCNTs.[25,26] Electron donating effect of the bases was even enhanced without the attraction from the backbone charges. Therefore, the C1s peak further up-shifted. After acid treatment for 8 h, the main C1s peak shifted back because of the p-doping effect of nitric acid.

The interaction between SWCNT and DNA and the effect of acid treatment were also characterized by Raman spectra. The G-band shifted to a higher frequency (blue shift) after p-doping and to lower frequency (red shift) after n-doping according to previous reports.[33] As shown in Fig. 7, the G band slightly red shifted (about 3 cm^{-1}) for SWCNT-DNA films compared to

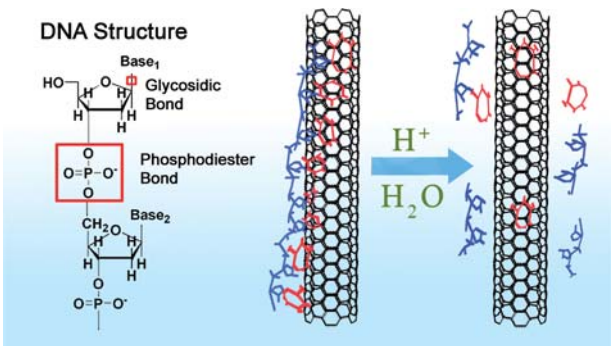

Fig. 6 Schematic diagram of the degradation and removal of DNA from SWCNT; Blue chains, DNA backbone; Red rings, DNA bases.

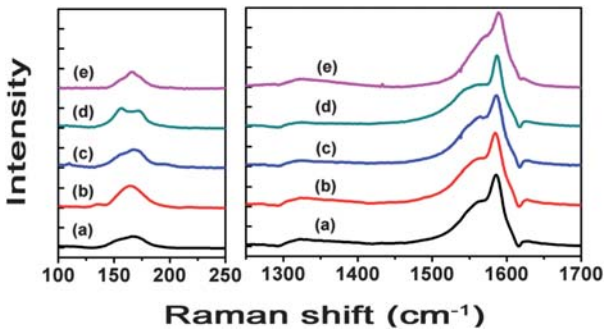

Fig. 7 Raman spectra of (a) SWCNT-denatured DNA films prepared by filtration method; (b) 14 M nitric acid treatment for 1 h of (a); (c) SWCNT-denatured DNA films prepared by spray coating method; (d) 14 M nitric acid treatment for 8 h of (c); (e) reference film.

reference films, indicating electron transfer from DNA to SWCNTs as proved by XPS data.

Another noticeable point in Raman spectra was that the Breit–Wigner-Fano (BWF) line at about 1630–1650 cm^{-1} was enhanced for SWCNT-DNA films. The shape and intensity of the BWF lines were sensitive to the interactions among nanotubes in bundles, or between nanotubes and surrounding molecules.[17] In our case, the bundle size of SWCNTs in SWCNT-DNA films was smaller than that in reference films which were prepared by SWCNTs aqueous solutions without any dispersants. Therefore, the enhancement of BWF lines was attributed to strong interaction between SWCNTs and DNA molecules. No obvious difference on BWF peaks of SWCNTs films before and after acid treatment proved the unchangeable interaction between the adsorbed bases and SWCNTs. Radical breathing mode (RBM) often gave insights into the changes on the nanotube environment. The RBM peak broadened and slightly upshifted after the introduction of DNA, which testified the strong interaction between SWCNTs and DNA molecules.[34] It recovered after treatment with nitric acid for 1 h, indicating the removal of DNA. After 8 h acid treatment, the RBM region split into two peaks due to the doping effect. No obvious changes on the D-band demonstrated no further damage induced on tubes by acid treatment.

Conclusions

Both pristine and denatured DNA can disperse SWCNTs efficiently and the former was even more effective in the environment of low ionic strength. The interaction between SWCNTs and DNA molecules was strong and electrons were transferred from DNA to SWCNTs as characterized by XPS data and Raman spectra. Acid treatment could effectively remove DNA from SWNT films, and the sheet resistance decreased by a factor of 2.5–10 times with negligible change on the transmittance over the visible region. Denatured DNA molecules were more easily degraded and removed. Films with high performance (95 Ω/sq, 78%) and good stability have been obtained, which will have great potential applications as flat panel displays. The sheet resistance of SWCNT-denatured DNA films decreased after keeping the films in the air for several days, which may be due to the degradation of denatured DNA molecules by microorganisms in warm and humid air. This phenomenon provided an important inspiration for some effective, non-destructive and environmentally friendly routes to remove dispersants and will be studied further in future work.

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