Synthesis and Characterization of Processable Multi-Walled Carbon Nanotubes—Sulfonated Polydiphenylamine Graft Copolymers

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Water soluble and processable nanocomposites composed of multi-walled carbon nanotubes (MWNTs) and poly(diphenylamine sulfonic acid) (PDPASA) are synthesized and characterized. Two types of methodologies are adopted. MWNTs are covalently functionalized with 2,5-diaminobenzene sulfonic acid (DABSA) and further in situ polymerized with diphenylamine-4-sulfonic acid (DPASA). This results in the formation of nanocomposites, MWNT(DABSA)-g-PDPASA, in which PDPASA is presented as the graft chains onto MWNTs. In another approach, DPASA is in situ polymerized in presence of unfunctionalized MWNTs, results in a nanocomposite in which MWNTs are present as entrapped mass in PDPASA matrix. Both nanocomposites are found to be water soluble and can form free standing films. The conductivity of MWNT(DABSA)-g-PDPASA and MWNT/PDPASA is found to be 1.25 mS cm⁻¹ and 0.65 mS cm⁻¹, respectively, which is higher than that of pristine PDPASA (0.25 × 10⁻¹ S cm⁻¹). The nanocomposites are characterized for their structure, morphology, optical and thermal properties.

Keywords: Multi-Walled Carbon Nanotubes, Poly(diphenylamine sulfonic acid), Soluble, Processable, Nanocomposites.

1. INTRODUCTION

Carbon nanotubes (CNTs) have demonstrated a wealth of exceptional electrical, mechanical, and thermal properties that have made them useful for potential applications ranging from nano-electronics to biomedical devices.1 Recently, variety of conducting polymers has been tried for making CNT/polymer nanocomposites toward various target applications in order to obtain a new material that would possess synergic properties of CNT and polymer.2–4 The formation of CNTs/conducting polymer composites has proved to be a promising approach to the effective incorporation of CNTs into devices. Nanocomposites such as CNT/polypyrrole,5 CNT/polyaniline,6 CNT/polydiphenylamine,7 CNT/polythiophene,8 and CNT/poly(phenylene vinylene)9 have been prepared through chemical and electrochemical methods. However, CNT itself is insoluble in organic solvent or water, which makes it difficult to form thin films and films for applications. Considerable effort has been made on the preparation of soluble CNTs both in fundamental and applied research areas.10,11 Metallothionein proteins were trapped inside and placed onto the outer surfaces of open-ended MWNTs.11 Porphyrin was found to adsorb on SWNTs presumably via Van-der-Waals attraction between the nanotubes and porphyrin.12 Polyaniline covered MWNTs via acid–base reaction between emeraldine and MWNTs were also realized.13–15 However, issues such as dispersion/orientation, interfacial bonding, and nanotube deformation within matrix have still not been investigated in detail. In particular, the solubility and processability of the nanotubes, which are the prime factors for device applications, have not been achieved.

It is well established that sulfonated polyaniline derivatives are self-doped and are found to be soluble in water and other common organic solvents.16,17 Kim et al. synthesized water-soluble poly(4-anilino-1-butane sulfonic acid) by an electrochemical method.17 A water-soluble self-doped conducting poly(aniline-co-Ν-sulphopropyl aniline) was reported.18 Further, sulfonated polyaniline derivatives...
are known for their unique electrochemical and optical properties.\textsuperscript{19,20}

In the present investigation, we have prepared water soluble and processable multi-walled carbon nanotubes (MWN Ts)poly(diphenylamine sulfonic acid) (PDPASA) nanocomposites. MWN Ts were covalently functionalyzed with 2,5-diaminobenzene sulfonic acid (DABS A) and further polymerized with diphenylamine-4-sulfonic acid (DPASA). Also, DPASA is \textit{in situ} polymerized in presence of unfunctionalyzed MWN Ts. Both nanocomposites were found to be soluble in water. The nanocomposites were characterized for their structure, morphology, optical and thermal properties.

2. EXPERIMENTAL DETAILS

2.1. Materials

2,5-diaminobenzene sulfonic acid and diphenylamine-4-sulphonic acid sodium salt were from Aldrich, used as received. MWN Ts (10 \textendash; 50 nm in diameter, CNT Co., Ltd., Incheon, Korea) were rinsed with double-distilled water and dried. Cetyltrimethyl ammonium bromide (CTAB), N-methylpyrrolidinone (NMP), ammonium persulphate (APS) of analytical grade from Aldrich were used as received.

2.2. Functionalization of MWNTs

Following procedure was adopted for the preparation of diaminobenzene sulfonic acid functionalized MWNTs (MWNT-DABS A).\textsuperscript{21} 50 mg of MWNT was refluxed in 4 M HNO\textsubscript{3}, for 24 h and filtered through a polycarbonate membrane (0.2 \textmu m pore size). The residue, MWNT-COOH (carboxylated MWNTs) was washed with deionized water and dried under vacuum at 60 °C for 12 h. 50 mg of MWNT-COOH was refluxed in 100 ml of thionyl chloride at 65 °C for 24 h to get MWNT-COCI. MWNT-COCI was filtered, washed with THF and dried under vacuum at room temperature. To prepare the functionalized MWNTs, MWNT-COCI was refluxed with 2,5-diaminobenzene sulfonic acid using THF at 60 °C for 24 h. The functionalized MWNTs (MWNT-DABS A) were separated by filtration and dried under vacuum.

2.3. Preparation of Nanocomposites

Two types of methodologies were adopted for the preparation of nanocomposites of MWNTs and PDPASA. The typical polymerization procedure is outlined. To a solution of DPASA (40 mM) in 0.05 M CTAB, 20 mg of MWNT-DABS A was added and sonicated for 1 h. The mixture was cooled to 4 °C using a freezing mixture. A pre-cooled (4 °C) solution of ammonium persulphate (0.1 M) was added drop wise to the mixture with stirring and the mixture was stirred for 1 h. The resulting green precipitate, PDPASA grafted MWNT-DABS A (designated as MWNT(DABSA)-P-PDPASA) was filtered through a sintered glass crucible and washed. The composites were then dried under dynamic vacuum at room temperature.

In another approach, \textit{in situ} polymerization was carried out in the solution containing unfunctionalized MWNTs and DPASA using APS as oxidizing agent. The green precipitate, MWNT/PDPASA was formed, then filtered and dried.

2.4. Characterization

Fourier transform infrared (FT-IR) spectra of the nanocomposites were recorded using a Bruker IFS 66v FT-IR spectrophotometer in the region 400 cm\textsuperscript{-1} to 4000 cm\textsuperscript{-1} using KBr pellets. The morphology of the nanocomposites was examined by field emission scanning electron microscope (FESEM)—Hitachi S-4300 and field emission transmission electron microscope (FETEM)—JOEL JEM-2000EX with a field emission gun operated at 200 kV. Elemental compositions of the samples (% of carbon, nitrogen, hydrogen, and sulfur) were determined by Fison EA H10 elemental analyzer equipped with flash combustion furnace. The room-temperature conductivity of the free standing composites films was determined using the conventional two-point probe method. UV-Visible spectra were recorded using Varian UV-Visible spectrophotometer. Thermo gravimetric analysis was performed using a TA 2950 Hi-Res TGA at a heating rate of 10 °C/min under nitrogen atmosphere.

3. RESULTS AND DISCUSSION

MWNT/PDPASA nanocomposites were prepared by two methodologies. In one of the approach, MWNTs were functionalized with diaminobenzene sulfonic acid (MWNT-DABS A) and followed by \textit{in situ} polymerization of the solution containing MWNT-DABS A and monomer, diphenyalmine-4-sulfonic acid (DPASA). In another approach, polymerization of DPASA was carried out in presence of unfunctionalized MWNTs. Both methods yield soluble and processable conducting nanocomposites. However, the first approach resulted nanocomposites, in which poly(diphenylamine sulfonic acid), (PDPASA) is presented as a grafted chain onto MWNT(DABSA). PDPASA wrapped or coated MWNT was obtained in the other approach. There are few similarities and differences between the two types of MWNT/PDPASA nanocomposites.

Mechanisms that describe the formation of two types of nanocomposites prepared through \textit{in situ} polymerization of DPASA in presence of MWNT(DABSA) and unfunctionalized MWNTs are presented in Scheme 1. In the former case, it is anticipated that the amine groups present in MWNT(DABSA) and DPASA could be simultaneously oxidized by APS. As a consequence, a cross-reaction
could occur between the amine cation radicals formed from MWNT-DBASA and DPASA. This would result in the grafting of PDPASA onto MWNT-DABSA (Scheme 1(A)). However, in the later case of composite formation, grafting is not feasible (Scheme 1(B)), when polymerization of DPASA was carried out in presence of unfunctionalized MWNTs. Hence, a composite of MWNTs and PDPASA is expected.
It is interesting to note that both approaches of preparation of nanocomposites, MWNT(DABSA)-g-PDPASA and MWNT/PDPASA, yield soluble and processable conducting nanocomposites. Soluble and stable (green coloured) dispersion of the nanocomposites are resulted. On adding few drops of aqueous ammonia to a green solution in water, changes the solution colour from green to blue. Typical snapshots of solutions of MWNT(DABSA)-g-PDPASA dissolved in water before and after addition of ammonia are presented in Figure 1(i). Also, it is noted that blue solution was also stable. There was no settling of agglomerates in the solution.

Further, the neutralized composites are soluble in N-methylpyrrolidinone (NMP). Free standing films of MWNT(DABSA)-g-PDPASA are obtained by casting NMP solutions of MWNT(DABSA)-g-PDPASA onto glass, plate followed by drying at 50 °C for 2 h (Fig. 1(ii)). The free-standing blue film of neutralized MWNT(DABSA)-g-PDPASA could be transformed into a green film on exposure to HCl vapors (Fig. 1(ii)).

The elemental analysis (EA) results of MWNT(DABSA)-g-PDPASA and MWNT/PDPASA are presented in Table I. A 85% of grafting percentage of PDPASA was achieved. A 17% (w/w) of SWNT in the SWNT-poly(m-aminobenzene sulfonic acid) was reported. The grafting efficiency was calculated as 42.2% from the EA results (Table I).

A comparative account of the structure, morphology, optical and thermal properties of the nanocomposites (MWNT(DABSA)-g-PDPASA, MWNT/PDPASA) are presented.

### 3.1. FT-IR spectroscopy

FT-IR spectroscopy was used to characterize the chemical composition of the nanocomposites. FT-IR spectra of MWNT(DABSA)-g-PDPASA, MWNT/PDPASA and PDPASA are compared. FT-IR spectrum of PDPASA (Fig. 2(c)) shows sharp peaks at 1587 and 1488 cm\(^{-1}\) corresponding to oxidized form of PDPASA consisting of diphenoquinodimine (quinoid) and diphenyl benzidine (benzenoid) structures. The presence of band around 1150 cm\(^{-1}\) is attributed to the presence of diphenoquinone type units. The absorption band around 3390 cm\(^{-1}\)
correspond to -NH stretching mode of secondary amine. The band around 1306 cm$^{-1}$ is assigned to stretching vibration of C–N groups with partial double bond characteristics. Further, PDPASA shows peaks at 1010 and 1088 cm$^{-1}$, which corresponds to symmetric and asymmetric stretches of sulfonic acid groups in PDPASA, respectively. FT-IR spectra of MWNT(DABSA)-g-PDPASA and MWNT/PDPASA (Figs. 2(a, b)) show prominent peaks at 3395, 1300, 1480, 1595, and 1010 cm$^{-1}$, which are characteristics of doped PDPASA. Further, the band corresponding to the stretching of B–NH$^+\equiv Q$ (1150 cm$^{-1}$) showed variation in position and intensity between MWNT(DABSA)-g-PDPASA and MWNT/PDPASA. Typically, the shift in position is more pronounced in MWNT(DABSA)-g-PDPASA (1172 cm$^{-1}$) than in MWNT/PDPASA (1160 cm$^{-1}$). Hence, we anticipate that B–NH$^+\equiv Q$ groups in PDPASA might have interactions with MWNTs. This can happen by grafting of PDPASA chains onto MWNTs through reactions with -NH groups present in DABSA.

3.2. Morphology

Morphology of the nanocomposites was determined through field emission scanning electron microscopy (FESEM) and field emission transmission electron microscopy (FETEM) measurements. Figure 3 shows the FESEM images of MWNT(DABSA)-g-PDPASA and MWNT/PDPASA. The diameter distribution of the nanocomposites is presented. Strikingly, MWNT(DABSA)-g-PDPASA shows a narrow distribution of diameters with average diameter around 55 nm. On the other hand, MWNT/PDPASA has different distributions of diameters. Particularly, the average diameter is higher (~70 nm) than that noticed for MWNT(DABSA)-g-PDPASA. Hence, it is concluded that a compact coating of PDPASA is present in MWNT(PDASA) than in MWNT/PDPASA. Also, the coating of PDASA is uniform in MWNT(DABSA)-g-PDPASA (Fig. 3(a)). However, in the case of MWNT/PDPASA (Fig. 3(b)), an uneven or roughed coating of PDASA over MWNTs is observed.

FETEM images of the nanocomposites also informed that PDPASA was formed over MWNTs as a layer on both cases. In the case of MWNT/PDPASA (Fig. 4(b)), the composite had a microstructure in which MWNT was presented as entrapped mass in PDPASA matrix. Formation of a smooth layer of PDPASA on the surface of MWNT-DABSA was noticed in the case of MWNT(DABSA)-g-PDPASA (Fig. 4(a)). Compared with MWNT/PDPASA,
3.3. Conductivity Measurements

Conductivity measurements of the free standing films of MWNT(DABSA)-g-PDPASA and MWNT/PDPASA was made at 25 °C. The conductivity of MWNT(DABSA)-g-PDPASA and MWNT/PDPASA was found to be 1.25 mS·cm⁻¹ and 0.65 mS·cm⁻¹, respectively. The observed conductivity for the nanocomposites is higher than that of PDPASA (0.25 × 10⁻⁵ S·cm⁻¹).

3.4. XRD Analysis

The structural characteristics of the MWNT(DABSA)-g-PDPASA, MWNT/PDPASA was analyzed by X-ray powder diffraction measurements and the XRD profiles are shown in Figure 5. MWNTs exhibit the typical peaks at 25.2, 44.3, 55.6, and 74° corresponding to the graphite (002), (100), (101), (004), and (110) reflections, respectively. PDPSA shows a strong peak at 21.8°, a characteristic peak of its doped form (Fig. 5(d)). XRD profiles of MWNT(DABSA)-g-PDPASA and MWNT/PDPASA are similar to one observed for PDPASA, suggesting that the MWNTs were entirely encapsulated by PDPASA. Also, MWNT(DABSA)-g-PDPASA and MWNT/PDPASA exhibits peak around 25.2°, which is a characteristic of (002) graphite reflection. Both, MWNT(DABSA)-g-PDPASA and MWNT/PDPASA display typical peaks of the emeraldine salt form of PDPASA with suppressed intensities of the peaks of MWNTs.

3.5. UV-Visible Spectroscopy

Figure 6 shows the UV-Visible spectra of MWNT(DABSA)-g-PDPASA, MWNT/PDPASA and PDPASA in NMP solution. UV-Visible spectrum of PDPASA shows the characteristic bands around 330 and 650 nm (Fig. 6(c)). The band observed at 330 nm is due to the inter-band transition (π–π*), whereas the peak at 550 nm is assigned to the n–π* transition from the non-bonding nitrogen lone pair to the conduction band (π*). The UV-Visible spectra of MWNT(DABSA)-g-PDPASA, MWNT/PDPASA in NMP solution are also presented (Figs. 6(a) and (b), respectively). A more pronounced shift of the n–π* transition
in the spectrum of MWNT(DABSA)-g-PDPASA is witnessed than for MWNT/PDPASA. This infers that the MWNTs are not only embedded in a PDPASA molecule, rather MWNTs act as a dopant for PDPASA, which resulted in the bathochromic shift of π-π* band, from 550–605 nm. A similar kind of dopant effect was reported in MWNT-OSO3H/PANI composites. Also, a new band was observed around 330 nm for both composites and that may be attributed to π-π* -staking interactions between graphitic MWNTs and phenyl rings in PDPASA.

### 3.6. Thermal analysis

Thermal transitions of MWNT(DABSA)-g-PDPASA, MWNT/PDPASA, MWNT, and PDPASA, were recorded by the thermogravimetric analysis under N2 atmospheric. Further, TGA was used to estimate the amount of PDPASA present in the nanocomposites. The amount of grafting to MWNTs in the composite was determined from the weight loss of the composite at 400 °C. Thermogram of MWNTs displays steady without evident weight loss below 600 °C. On the contrary, MWNT(DABSA)-g-PDPASA and MWNT/PDPASA, show three major weight loss (Table II). The first two weight losses observed at 160 °C and >320 °C corresponding to the removal of dopants and degradation of backbone units, respectively. As for PDPASA, the first two loss stages in the temperature range 100–160 °C is presumably due to the elimination of water and the loss of dopant. The third weight loss up to 270 °C are attributed mainly to the release of solvent. Above 380 °C, decomposition of PDPASA was noticed. It is interesting to note that more amount of PDPASA is present in MWNT/PDPASA (58%) than in MWNT(DABSA)-g-PDPASA (43%). The presence of more amount of PDPASA in MWNT/PDPASA is consistent with the observation made through FETEM.

### 4. CONCLUSIONS

In summary, we have prepared water soluble and processable nanocomposites composed of multi-walled carbon nanotubes (MWNTs) and poly(diphenylamine sulfonic acid) (PDPASA) with two different morphologies. The nanocomposites are found to be soluble in water and other common organic solvents. Further, it is demonstrated that the nanocomposites can be formed as free standing films, and the films can be easily transformed from conducting (green) to non-conducting (blue) form. These nanocomposites are expected to find wide range of applications in electrochromic devices, sensors, etc.

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### References and Notes


### Table II. Summary of the thermal behavior of the nanocomposites.

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<tr>
<th>Samples</th>
<th>Temperature range (°C)</th>
<th>Weight loss (%)</th>
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<tbody>
<tr>
<td>MWNT</td>
<td>600–800</td>
<td>32.5</td>
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<tr>
<td>MWNT(DABSA)-g-PDPASA</td>
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<td></td>
<td>320–380</td>
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<td></td>
<td>380–800</td>
<td>70.0</td>
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