Dispersion of Single-Walled Carbon Nanotubes for Display Applications

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Abstract

Dispersion of arc-discharged single-walled carbon nanotubes (SWNTs) has been accomplished by a water soluble polymer wrapping functionalization at room temperature. The treated SWNTs were redispersed in both aqueous and many organic solvents and the solutions were found to be stable.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have a great deal of potential for nanoscale device applications including large area transparent electrodes [1,2], solar cells [3], flat and flexible displays [4] owing to their novel electronic, structural and mechanical properties. However, a number of challenges must be overcome before SWNTs can be exploited for most of these envisioned applications. One of the crucial problems in realizing these applications is that, while the majority require individually dispersed nanotubes, SWNTs tend to aggregate forming bundles due to their long aspect ratios (>1000) and the strong anisotropic interactions between them (0.5 eV nm^{-1}) [5].

Numerous attempts have been made to develop an effective method to debundle and discretely disperse SWNTs. These strategies have involved covalent chemical functionalization of the tubes' sidewalls, scission of tubes by mechanical milling [6], coating of surfaces of the tubes using surfactants [7], small organic molecules and macromolecules [8]. These methods are not ideal since the chemical processing of SWNTs often damages their structure and the physical shortening which in turn affect the properties of SWNTs [5].

In this paper, we present results from a systematic study on the effects of a water soluble polymer wrapping functionalization of arc-derived bundles of SWNTs to generate solutions containing individual SWNTs. The impact of our chemical and ultrasonic processing on the structural order of the nanotubes has been studied by Raman spectroscopy. A centrifuge was used to separate the light and heavy fractures and thus small and large diameter SWNTs. Using scanning electron microscope (SEM) we have studied the distribution of the tubes/bundles and the results are presented here.

2. Experimental details

Arc-discharge SWNTs purchased from Iljin Nanotech (ASP-100F) was used for the present investigation. As the majority of amorphous carbon, carbon nanoparticles and metal catalysts were removed by both gas phase oxidation and acid treatment, it reaches the purity of 90 volume percent. The as delivered material was found to contain bundles typically with ~20s of SWNTs, ~5-10 μm long with a range of nanotube diameter (d_t) ~1.2 to 1.4 nm, as determined by high resolution transmission electron microscope (HRTEM), SEM and Raman-active radial breathing modes (RBM).

Ultrasonic sound was used to debundle and disperse the above SWNT bundles in a polymer added aqueous solution. In the typical experiment, the SWNT:

polyvinylpyrrolidone (PVP) : deionized (DI) water (18.2 MΩcm) was used in the weight ratio 10 : 2 : 2000 respectively. The PVP purchased from Sigma-Aldrich (typical Mw 29,000) was used. Ultrasonic dispersion was carried out for 5 h using a ultrasonic probe (Sonics Vibra Cell). The solution was then immediately centrifuged at 14,000 rpm for 90 min. and the supernatant liquid containing the debundled SWNTs, was withdrawn for analysis. Thus, the large particles and a few large bundles were (>10 nm) removed.

The quality of the dispersion of isolated tubes in DI water was examined by SEM. In addition to that, a thin mat of carbon nanotube film (bucky paper) was formed from the SWNT dispersed solution on a isopore membrane filter (200 nm pore size, GTTP) and dried under vacuum after several washing with DI water and finally with absolute ethanol. Then, the treated SWNTs were redispered in DI water, ethyl alcohol (ETOH), N-methyl-2-pyrrolidone (NMP) and 1,2-dichloroethane (DCE) by transferring the SWNTs from the bucky paper.

3. Results and discussion

During the sonication process, small air bubbles were released from the solution indicates the debundling of SWNTs. The debundling is being made due to effective wetting by the polymer wrapping functionalization of the sidewalls of the SWNTs. Figure 1 shows the SEM images of the SWNTs before (a) and after (b) the treatment. It is clear that the centrifuged supernatant (Figure 1 b) contains many individual SWNTs along with a few small bundles. Further, it is to be noted that once we redisperse the SWNTs from the bucky paper (Figure 2) in DI water, ETOH, NMP and DCE, a quantity of black powder spontaneously precipitated after two days from dispersion with the resultant supernatant being stable, homogeneous and appears as dark color as shown in Figure 3.

Room temperature micro Raman spectra (514.5 nm excitation) of SWNTs before and after the polymer treatment are shown in Figure 4. The RBM Raman features (150-220 cm^{-1}) are used to calculate nanotube diameters following the expression d_t (nm) = 223.5 cm^{-1} nm / [ω_{RBM} (cm^{-1}) – 12.5] [9]. The observed Raman spectra in the present investigation look like a Gaussian diameter distribution centered on a mean diameter of 1.295 nm. This is the mere indication for our sample composed of all the possible (n,m) nanotubes (real samples) that usually exhibit a Gaussian diameter distribution around some mean diameter. The broadening (>30 cm^{-1}) has been observed to increase as the SWNT diameter is increased. The increase of broadening from the centrifuged bottom reflects the increase of SWNT diameter confirms the presence of large diameter SWNT at the centrifuged bottom.

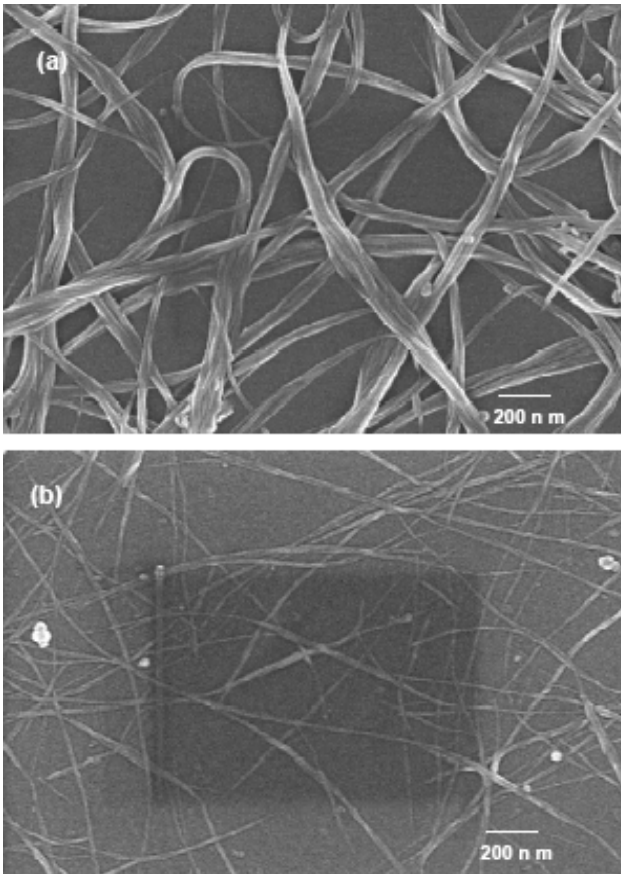


Fig. 1. SEM images of as prepared SWNTs (a) and treated SWNTs (b) obtained by dispersing them in DI water.

The observation of characteristic multi peak features around 1570 and 1590 cm^{-1} also provides a signature of SWNTs. Spectra in this frequency range were used for SWNT characterization, independent of the RBM observation. This multi-peak feature was also used for diameter characterization although the information provided is less accurate than the RBM feature, and it gives information about the metallic character of the SWNTs in resonance with a given laser line. Unlike graphite, the G band in SWNTs

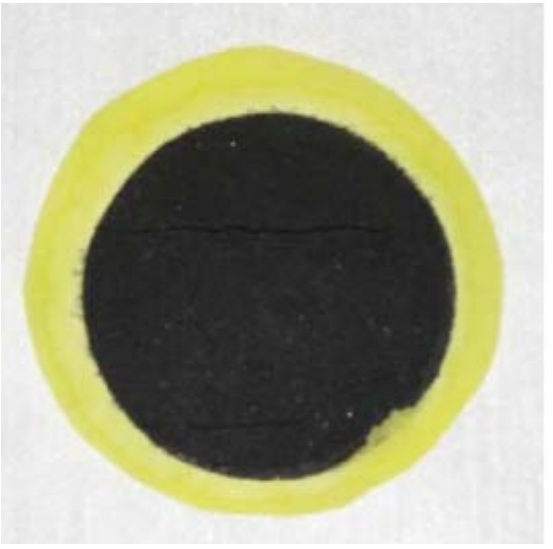


Fig. 2. Photo image of a uniform 4.7 cm diameter carbon nanotube film (dark region) on a 200 nm GTTP membrane filter.

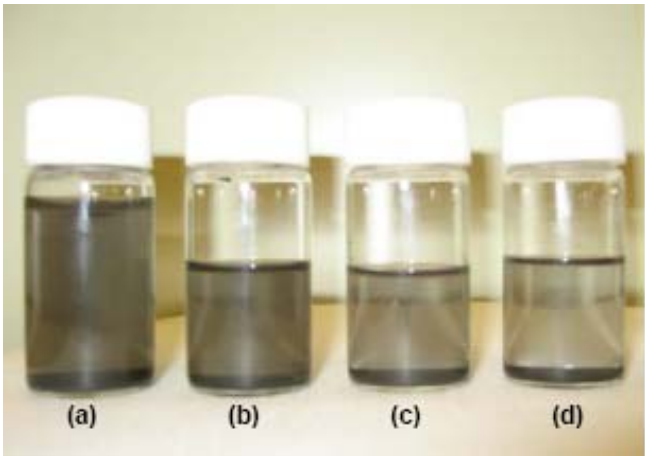
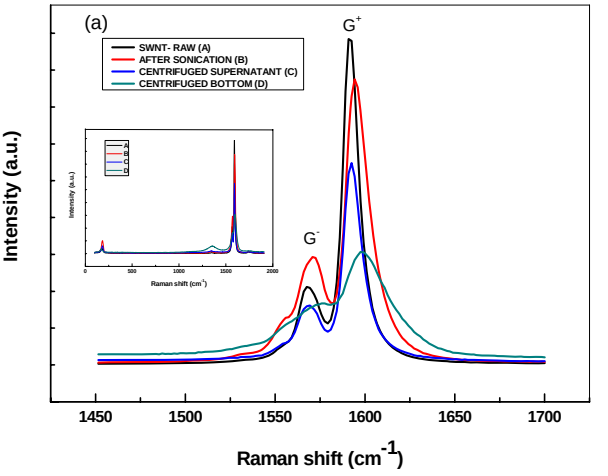


Fig. 3. Vials containing redispersed SWNTs 0.1 mg ml^{-1} in DI water (a), redispersed SWNTs 0.15 mg ml^{-1} in NMP (b), ETOH (c) and DCE (d) - imaged after one week and black precipitate clearly seen on the bottom with the resultant supernatant.

gives rise to a multi-peak feature, also named the G band. A simple analysis has been carried out considering the two most intense G peaks labeled as G^+, for atomic displacements along the tube axis and G^-, for modes with atomic displacement along the circumferential direction, and the lowering of the frequency for the G^- mode is caused by the curvature of the nanotube which softens the tangential vibration in the circumferential direction. The difference between the G band line shape for semiconducting and metallic SWNTs is evident in the line shape of the



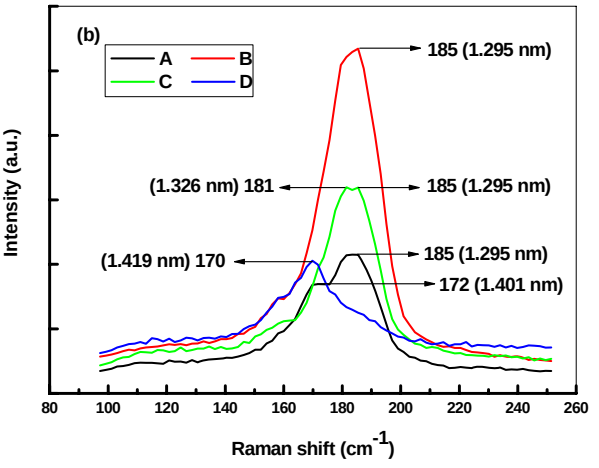


Fig. 4. Raman spectra showing G-band (a) and RBM (b) features of (A) SWNT –raw (B) after the PVP treatment (C) centrifuged supernatant and (D) centrifuged bottom. The inset in (a) shows the RBM, G and D peaks.

G^- feature, which is broadened for metallic SWNTs (Breit-Wigner-Fano) in comparison with the Lorentzian lineshape for semiconducting tubes, and this broadening is related to the presence of free electrons in nanotubes with metallic character. The Breit-Wigner-Fano (BWF) line is observed in many graphite-like materials with metallic character, such as n-doped graphite intercalation compounds (GIC), n-doped fullerenes as well as metallic SWNTs [10]. Moreover, it is identified that the diameter dependence of the G^+ frequency (ω_{G+}) and the G^- frequency (ω_{G-}) for metallic and semiconducting SWNTs. While ω_{G+} is practically independent of tube diameter, ω_{G-} decreases when decreasing d_t and this decrease becomes larger as the curvature of the sheet increases.

The splitting $\Delta\omega_G$ for centrifuged supernatant and bottom were 24 cm^{-1} and 25 cm^{-1} respectively. Further, the dwindle in peak position ω_{G-} about 4 cm^{-1} for supernatant from bottom is the indication of decrease in d_t of SWNTs.

The increase in intensity of D-peak for centrifuged bottom compared with the other samples indicates the presence of amorphous carbon/bad resonance condition. It is to be noted that the broad feature arising from the presence of amorphous carbon and the reduction of D-band frequency ω_D about 3 cm^{-1} for supernatant SWNTs over bottom further represents the decreasing tube diameter.

4. Conclusion

In conclusion, we have developed an efficient process for the stable dispersion of arc-discharged SWNTs in both aqueous and organic solvents. Raman analysis substantiates the pristine tube structure of the PVP wrapped SWNTs. Above all, this treatment is less expensive, simple and potentially scalable. The dispersed SWNTs will be useful to make devices for display applications

5. References

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