

Functionalization of Carbon nanotubes and study of its optical and structural properties

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Received: March 30, 2007, Accepted: April 07, 2007

Abstract: We have studied the effect of chemical functionalization on the structural and optical properties of single walled carbon nanotube grown by chemical vapor deposition. Functionalization process is performed in aromatic amine solvent at a temperature of 184^o C. The functionalization process results in exfoliation of large bundles of SWNTs and solubility is greatly enhanced. X-ray diffraction (XRD) and Scanning electron Microscopy (SEM) results show significant changes in the structure and morphology of the CNTs after functionalization. Change in nature of bonding and impurities in CNT are studied using FTIR spectroscopy. UV-visible absorption studies show strong absorption peak below 400 nm and a broad peak at 450 nm after functionalization. Strong visible fluorescence peaks at 568 nm and 608 nm are observed at room temperature after functionalization of SWNTs. Fluorescence energy is found to be dependent on excitation wavelengths. Possible origin of visible fluorescence from functionalized nanotubes is discussed.

Keywords: Carbon nanotubes, solubility, functionalization, fluorescence

1. INTRODUCTION

Carbon nanotubes (CNTs) have been the subject of intense research in recent years because of their unique electronic, mechanical, and physical properties [1-3]. Some solution properties of CNTs have also been studied aimed at their chemical modification and functionalization [4-8]. However, the low solubility of CNT in most organic solvents limits their chemical manipulation, quantitative characterization, and wider application. Several methods have been reported to solubilise CNTs [9-11] including attachment of long alkyl chains [4] and admixture with polymers [5, 6]. Strong luminescence of solubilized carbon nanotubes after functionalization with polymers has been reported [5]. Amine functionalization of nanotubes based on amidation of carboxylic acid groups of COOH-functionalized SWCNT has been reported by Gabriel et. [7, 12]. Some of the recent studies shows accelerated aniline functionalization in case of multiwalled carbon nanotubes (MWCNTs) with the application of microwave power [13]. In this paper, we report the dissolution of pristine single walled carbon nanotubes (SWNTs) in aromatic amines and changes in their chemical, structural and optical properties. In particular, changes in the chemical and optical emission and absorption properties are discussed in details.

2. MATERIAL AND METHODS

2.1. Experimentation Techniques

For the present study, we used commercially procured single walled carbon nanotubes (SWNTs) grown by chemical vapor depo-

sition. These SWNTs are basically bundled thin walled nanotubes of diameter ~2 nm, length 5-15 μ m, and purity >50%. The pristine samples are in the form of black powders. The SWNT samples are first dispersed in aniline using an ultrasonicator and subsequently subjected to reflux reaction. These SWNTs were filtered through a filter membrane to produce the so-called 'bucky paper'. In a typical experiment, 40 mg of accurately weighed SWNTs were added to 5 ml of aniline and then the mixture was refluxed at 184^o for 3 hours in dark. Dissolution of SWNTs in aniline can be observed by the color change of the solution after reflux for a shorter time. Thus, with continuous heating, the original colorless aniline solution became brownish and then turned dark red. After cooling to room temperature, a CNT solution was obtained by filtration through a filter paper. The solubility of SWNT in aniline is up to 8 mg/mL [14]. This aniline-SWNT solution can be readily diluted with other organic solvents such as acetone, toluene and methanol. We have collected functionalized SWNT (F-SWNT) by filtration using 0.2 PVDF membrane filter paper. Filtered solution and filtrate remaining over the filter paper (termed as 'bucky paper') both were used for characterization.

2.2. Characterization Techniques

Structure and morphology of these SWNTs are studied by X-ray diffractometer (Bruker, Advance D8) and digital scanning electron microscope (LEO 1430 VP). Room temperature fluorescence measurements were performed with 450 nm and 500 nm excitation sources using a commercial Fluorimeter (Thermo Electron, FA-357). UV-Vis absorption measurements were performed in the range 200-800 nm using standard Spectrometer (Perkin-Elmer, Lambda-45). FTIR measurements were performed in the range

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400–4000 cm^{-1} using FTIR spectrometer (Perkin-Elmer Spectrum one) .

3. RESULTS AND DISCUSSION

3.1. XRD

Figure 1 shows the XRD pattern of pristine, F-SWNT on filter paper and F-SWNT in the filtered solution. Bucky paper sample show broadening of peak and reduced intensity in the XRD pattern when compared with the pristine sample.

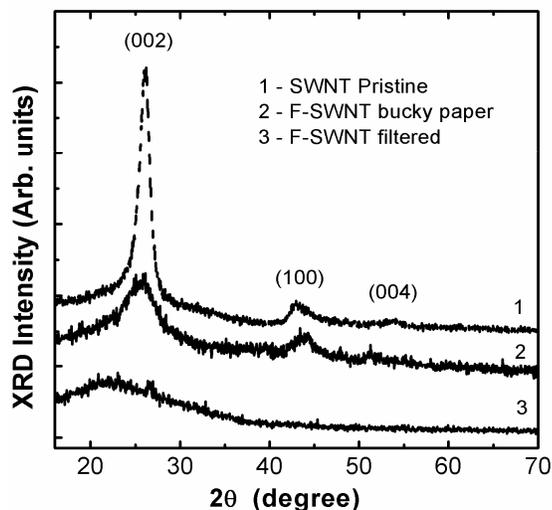


Figure 1. XRD pattern of pristine SWNTs and F-SWNTs functionalized with aromatic amine.

However, functionalized SWNTs show only (002) peak with very broad peak with much lower intensity and the peak is shifted to lower 2θ value than the pristine sample, and absence of (100) and (004) peaks. Peak broadening and peak shift indicate that the strain is introduced in the nanotube structure due to surface functionalization and introduction of defects during reflux reaction. Another possible reason for peak broadening is that the filtered solution contains nanotubes of smaller diameter, since XRD line width is inversely proportional to the diameter of the nanotubes. Since the solubilized SWNTs have reacted with the amine solvent during functionalization, the structure is modified at the surface of the nanotube and hence a change in the XRD pattern.

3.2. SEM

SEM images (see fig. 2) show that after functionalization, CNTs are bundled together and tubes are less isolated and distinct as compared to the pristine nanotubes. Fig: 2(a) shows an image for pristine nanotube and Fig, 2(b) and 2(c) show images for F-SWNTs. We found that as functionalized nanotubes are bundled together due to enhanced interaction among the tubes. Images shown in Fig 2(b) & Fig 2(c) are taken after dispersing the filtered product with Sodium dodecyl sulphate (1 wt %) under sonication for 30 minutes. In Fig: 2(c) arrow 1 indicates the ropes of nanotubes, 2 indicates that quite a few of the low diameter tubes were seen isolated while region indicated by 3 shows the mesh of nanotubes formed after functionalization. From Fig 2, it is evident that

tubular structure of nanotubes was intact even after functionalization.

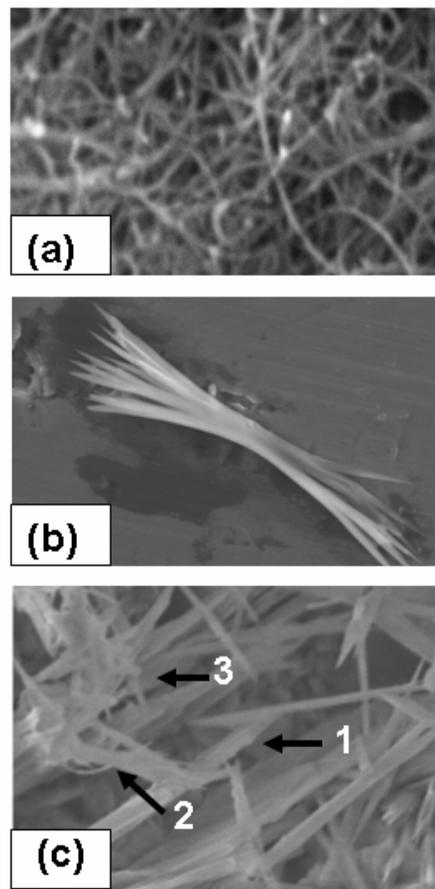


Figure 2. (a)SEM images of SWNTs before functionalization, (b) SEM image of SWNTs after functionalization, (c) magnified image of a portion of image (b). Arrows in Fig 2(c) shows: 1-Bundled nanotubes, 2- individual nanotube, and 3 - aggregated nanotube bundles.

3.3 Absorption Spectra

Pristine SWNTs dispersed in common solvents (e.g. ethanol, methanol, acetone etc) do not show any optical absorption in the measured range (UV-Visible) at room temperature. However, after functionalization strong optical absorption peak below 350 nm and a relatively broad absorption band at ~ 440 nm is observed in UV-Vis spectra as shown in Fig. 3(a). Absorption spectrum of aniline solution is shown for comparison, since aniline is used for functionalization. Dilution of functionalized nanotube solution with acetone shows stronger absorption peak at ~ 440 nm irrespective of concentration of acetone, as shown in Fig. 3(b).

The broad peak at ~ 440 nm is attributed to the formation of an aniline-SWNT charge transfer complex [11,14]. Carbon nanotube is expected to be a good electron acceptor while aniline is a fairly good electron donor [5,15]. At elevated temperature (~ 184 °C), CNTs and aniline may form a charge-transfer complex in its ground state as evidenced by the appearance of new absorption peak in the visible region. SWNT-aniline solution diluted with toluene and chloroform shows maximum absorption at wavelength 301 nm and dilution in acetone showed peak absorption at 323 nm.

Intensity of absorption in SWNT-aniline diluted with toluene and chloroform is found to be much higher than the dilution with acetone. A mechanism proposed by Sun et al. [14] for attachment of alkyl amine with carbon atoms of nanotubes is likely to operate during the reflux reaction performed in the present study. Results of our FTIR studies (shown later) confirms such a reaction where C-H and C-N bonds are found after reaction. In general, nanotubes have a strong tendency to aggregate, which is one of the reasons they are insoluble in common solvents.

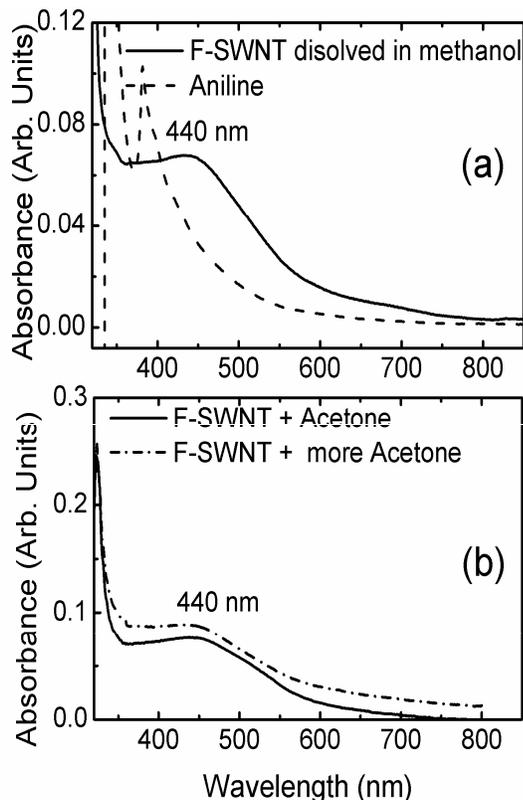


Figure 3. UV-Vis absorption spectra of F-SWNTs in different solvents.

3.4 Emission Spectra

Pristine samples do not show any measurable fluorescence signal in the visible region. However, after functionalization, strong visible fluorescence emission is observed from SWNTs. Figure 4 shows fluorescence spectra of the functionalized SWNT samples diluted in toluene and acetone. Figure 4 (a) shows two strong fluorescence peaks at 568 nm and 608 nm from functionalized SWNTs. The spectrum is obtained after subtracting the background due to toluene. Similar spectrum is obtained when acetone is used for dilution. Fig. 4(b) shows that fluorescence spectra are dependent on excitation wavelength. Higher the energy of excitation, additional higher energy or low wavelength peaks are observed in fluorescence spectra, which indicates that functionalized nanotubes have broad density of states.

It is well known that pristine SWNTs emit in the near IR range due to their small bandgap. However, functionalization modifies the surface and higher energy transitions are allowed due to possible opening of the bandgap. Fluorescence could be mediated by the defects at the nanotube surface after functionalization. Modification of nanotube surface is apparent from XRD pattern. However, pho-

toelectron spectroscopic measurements would be helpful in understanding details of the surface conditions. Nevertheless, such high fluorescence yield of F-SWNTs can be exploited for applications involving visible light emitting devices.

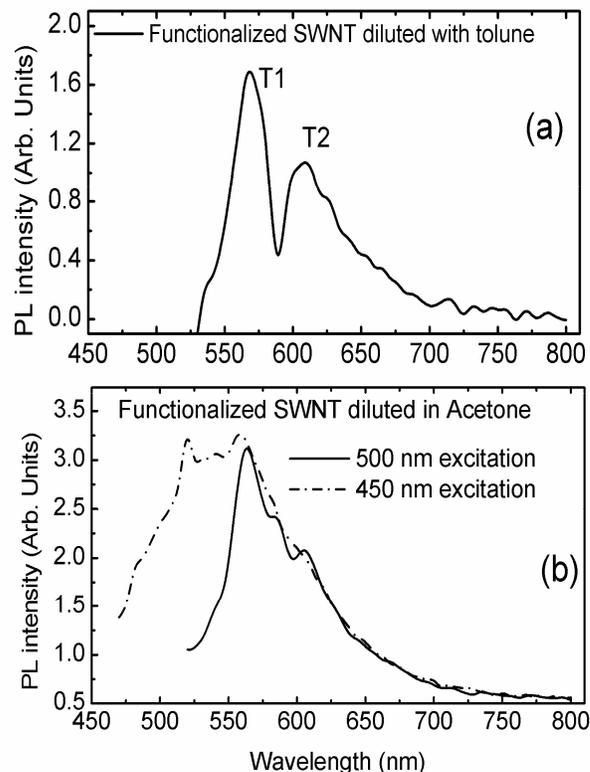


Figure 4. Room temperature fluorescence (PL) spectra of F-SWNTs. (a) Excitation with 500 nm, (b) Excitation with 450 nm and 500 nm light. 567 nm and 607 nm peaks are common to F-SWNTs diluted with various solvents.

3.5 FTIR Spectra

Figure 5 shows FTIR spectra of SWNT samples before and after functionalization. FTIR spectra of pristine samples show several bands, such as C-O stretching (1022), C-H deformation (1392), C-C stretching (1627), CO₂ (2358), C-H stretching (2917) and moisture related bands (3436). Due to long exposure in atmosphere, these samples show hydrogen and oxygen related bonds, besides the expected C-C band. Though energy dispersive X-ray (EDX) spectra do not show any measurable impurity content such as oxygen and hydrogen, FTIR spectra clearly show the presence of impurities in the nanotubes. Lower spectrum in Figure 5 shows the FTIR spectrum after functionalization. The spectrum of F-SWNTs shows several additional bands related to grafted aniline (chemical group). The strong absorption peaks at 1603 and 3358 are due to N-H deformation of primary amine and N-H stretching (asymmetric) vibrations, respectively. Small peak at 1053 is due to C-N stretching modes. Therefore, the amino group appeared to graft onto the surface of SWNTs. Amine group is believed to change the surface properties of the CNTs that in turn drastically changes the optical properties of the SWNTs as observed in fluorescence and optical absorption measurements. This is in contrast to the possible physical adsorption of impurities on the nanotube which may not alter the electronic properties of the material.

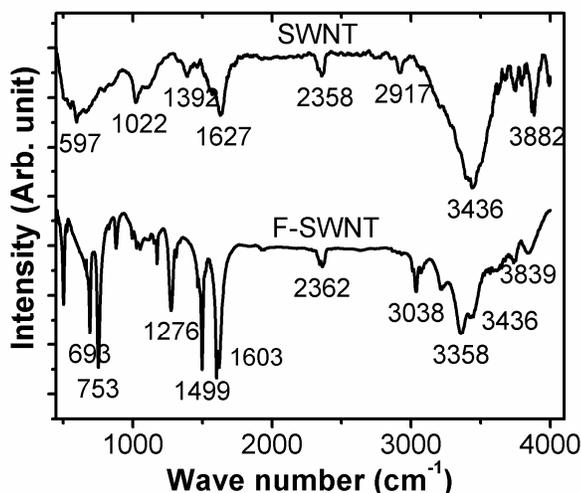


Figure 5. FTIR spectra of SWNTs before (upper curve) and after functionalization (lower curve).

It is likely that a new chemical species is produced on heating SWNT in aniline, and that photoexcitation of this species leads to a luminescent charge separated state (exciplex). In polymer bound carbon nanotubes, Riggs et al. suggested that the luminescence might be due to the trapping of the excitation energy at defect sites [5]. Another factor that might enhance the fluorescence efficiency is their large molecular size, which would inhibit deactivation through molecular motion. More studies would be required to pinpoint the detailed mechanism of visible fluorescence.

CONCLUSIONS

In conclusions, we have shown that carbon nanotubes can be dissolved in aniline without any prior chemical functionalization, and this material is then soluble in a variety of organic solvents. These soluble SWNTs exhibit visible fluorescence at room temperature and emission energy is excitation wavelength dependent. The solubility of CNTs has several implications. One among many important application is that one can envisage CNT-aniline solutions for

the formation of nanocomposites or thin films, which would solve some of the practical problems involved in making nanotube based electronic and field emission devices. The amino functionalized nanotubes can be used for binding various types of materials including polymers and biological systems. The strong visible fluorescence emission of CNTs should be a useful probe in elucidation of the physical and biological properties of these materials.

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