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Covalent and non-covalent functionalization and solubilization of double-walled carbon nanotubes in nonpolar and aqueous media[†]

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Abstract. Double-walled carbon nanotubes (DWNTs) have been functionalized by both covalent and non-covalent means. Covalent functionalization has been carried out by attaching an aliphatic amide function to DWNTs which enable solubilization in non-polar solvents. Solubilization in non-polar solvents has also been accomplished by non-covalent functionalization by using 1-pyrenebutanoicacid succinimidyl ester (PYBS). Non-covalent functionalization of DWNTs has been carried out by using polyethylene glycol (PEG) and polyoxyethylene(40)nonylphenyl ether (IGPAL), both of which enable solubilization in aqueous media. These functionalized DWNTs have been characterized by transmission electron microscopy, IR and Raman spectroscopy.

Keywords. Carbon nanotubes; double-walled nanotubes; functionalization; Raman spectroscopy; transmission electron microscopy.

1. Introduction

Functionalization and solubilization are important aspects of the chemistry of carbon nanotubes (CNTs), these chemical manipulations being essential for many of the applications of CNTs.[1–5] Multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) have been functionalized by both covalent and non-covalent means.[1,6–16] The covalent functionalization method typically involves acid treatment of the CNTs followed by reaction with thionyl chloride followed by reaction with a long chain amine. Such amidation gives rise to SWNTs soluble in non-polar solvents.[1–4,8,10] Other methods such as fluorination have also been used for the functionalization of SWNTs.[1,17] Covalent functionalization, however, has the limitation in that it drastically affects the electronic structure of the SWNTs and hence affects their properties. Non-covalent functionalization of CNTs has been carried out by employing surfactants, aromatics and other reagents.[12,13,18]

We have been interested in the functionalization and solubilization of double-walled carbon nanotubes (DWNTs) by both covalent and non-covalent means, specially because functionalization of DWNTs should affect only the outer nanotube surface, leaving the inner tube intact. This feature is attractive with inherent technological applications. We have therefore carried out the functionalization of DWNTs by both covalent and non-covalent means. We have carried out covalent functionalization employing the amidation reaction, giving rise to DWNTs soluble in non-polar solvents. In the case of non-covalent functionalization, π–π interactions through bezinoid groups and the interaction with polymers give high degree of solubility for carbon nanotubes even at low level of functionalization. Thus, we have carried out functionalization of DWNTs non-covalently not only by wrapping the long chain polymers such as polyethylene glycol (PEG) and polyoxyethylene(40)nonylphenyl ether (IGPAL) but also through the π–π interactions with 1-pyrenebutanoic acid succinimidyl ester (PYBS). Functionalization of DWNTs with PYBS enables the solubilization in non-polar solvents whereas functionalization with IGPAL and PEG enables the solubilization in water.

2. Experimental

2.1 *Covalent and non-covalent functionalization of DWNTs*

DWNTs were prepared by the catalytic chemical vapour deposition process following the procedure

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[†] Dedicated to Prof. C N R Rao on his 75th birthday
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described earlier.[19] To solubilize DWNTs in non-polar solvents, the following procedure was employed. In the first step, acid treated DWNTs were prepared by the following procedure. Concentrated nitric acid (1 ml) and water (15 ml) were added to DWNTs (10 mg) in a teflon lined autoclave and subsequently heated in a microwave oven for 10 min under hydrothermal conditions. Further, the Teflon autoclave containing sample was heated at 100°C for 12 h. The product was washed with distilled water and centrifuged repeatedly to remove traces of acid. This yielded DWNTs that was functionalized with –OH and –COOH groups. The acid treated DWNTs were refluxed with excess $SOCl_2$ for 12 h and the unreacted $SOCl_2$ was removed under vacuum at room temperature. This product was treated with dodecylamine (5 ml) in an autoclave under solvothermal conditions at 100°C. We adopted another procedure to solubilize DWNTs in non-polar solvents. The reaction procedure is as follows. Excess amount of PYBS (5 mg) was added to 1 mg of DWNTs in a test tube, which was heated at 150°C for 10 min. The resulting mixture was dispersible in dimethylformamide by ultra sonication for 30 min. The resulting suspension is stable for several hours.

In order to solubilize DWNTs in water, we functionalized DWNTs with polyethylene glycol (PEG) and polyoxyethylene(40)nonylphenyl ether (IGPAL). PEG-functionalized DWNTs was prepared by reacting acid treated DWNTs with excess of PEG (6 ml) and concentrated HCl (2 ml) under solvothermal conditions at 100°C for 12 h. IGPAL-functionalized DWNTs were prepared as follows. Excess amount of IGPAL (10 mg) was added to 2 mg of DWNTs in a test tube, which is heated at 100°C for 10 min. Distilled water was added to the resulting mixture and sonicated for 30 min. The resulting suspension is stable for more than 7 days.

2.2 *Characterization*

We have characterized the pure and functionalized DWNTs by various techniques. Field emission scanning electron microscope (FESEM) images were recorded with a FEI NOVA NANOSEM 600. Raman spectra were recorded with a LabRAM HR high-resolution Raman spectrometer (Horiba Jobin Yvon) using a He_Ne laser ($\lambda = 630$ nm). Transmission electron microscope images were obtained with a JEOL JEM 3010 instrument. IR spectra were recorded on KBr pellet with Bruker IFS-66V.

3. Results and discussion

Covalent functionalization of DWNTs was carried out by the amidation reaction employing the standard procedure.[1,8,10] In figure 1a, we show the infrared spectra of DWNTs at various stages of the functionalization process. After acid treatment, DWNTs show a carbonyl stretching band at 1720 cm^{-1} due to the presence of carboxyl groups. On functionalization with dodecylamine, the –C=O stretching band red shifts due to amide formation, in addition giving rise to –C–H and –N–H stretching bands around 2800 and 3400 cm^{-1} respectively and the CH_2 bending bond appear around 1420 cm^{-1}. Raman spectroscopy is highly useful to characterize DWNTs.[19,20] Figure 1b shows the Raman spectra of DWNTs in the radial breathing modes (RBM) region at various stages of the functionalization process. Pure DWNTs show the RBM bands in the 170–350 cm^{-1} region due to the inner wall tube breathing modes and bands below 170 cm^{-1} due to the outer tubes. The RBM bands of the inner tubes are affected only slightly on acid treatment and after amidation. The RBM bands of the outer tubes are, however, suppressed significantly after amidation as can been seen from figure 1b. Thus, the inner wall RBM bands of pure DWNTs are at 189 and 213 cm^{-1}. Which are shifted to 185 and 210 cm^{-1} respectively with acid treatment, and to 186 and 210 cm^{-1} respectively after amidation. There is a shift in the G band in Raman spectrum from 1575 cm^{-1} (pure DWNTs) to 1584 cm^{-1} after amidation. The D band shifts from 1310 to 1323 cm^{-1} after amidation with a slight increasing in intensity.

The amide functionalized DWNTs are dispersible in various organic solvents. In figure 2a, we show photographs of the dispersions of amide-functionalized DWNTs in dichloromethane and tetrahydrofuran. In figure 3b, we show a TEM image of DWNTs after covalent functionalization. The images are not as sharp after functionalization as in the case of pristine nanotubes (figure 3a), and the bundles seem to be intact. However, the images also revealed that the nanotube structure is not disturbed by functionalization.

Non-covalent functionalization of DWNTs was carried out by various ways. First, we used 1-pyrenebutanoicacid succinimidylester (PYBS) to functionalize DWNTs. This reagent has been used to functionalize SWNTs.[5] We observe a shift of the G band in the Raman spectrum from 1575 cm^{-1} (pure DWNT) to 1588 cm^{-1} after treatment with PYBS.

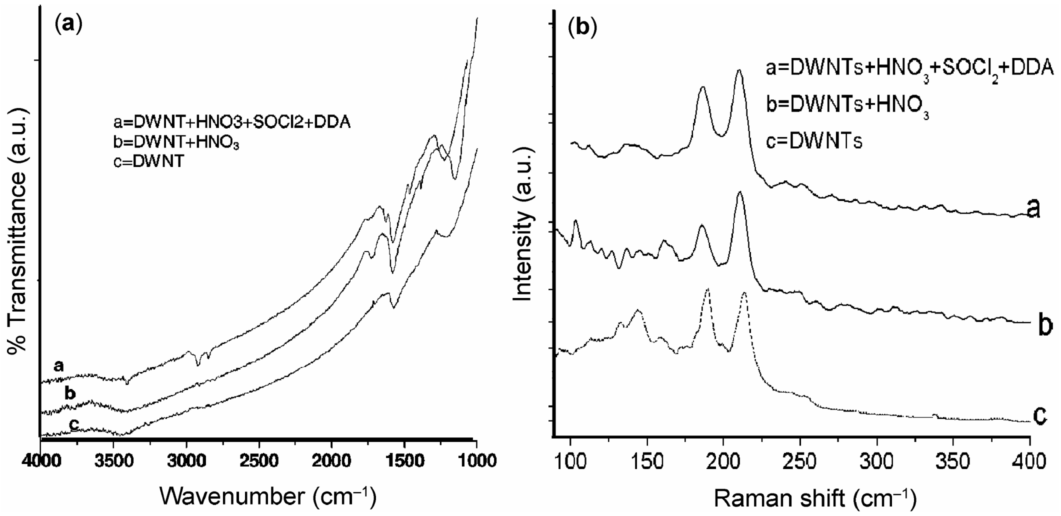

Figure 1. (**a**) Infrared spectra of DWNTs at various stages of covalent functionalization process through amidation. (**b**) Raman spectra showing the RBM bands of DWNTs at various stages of functionalization.

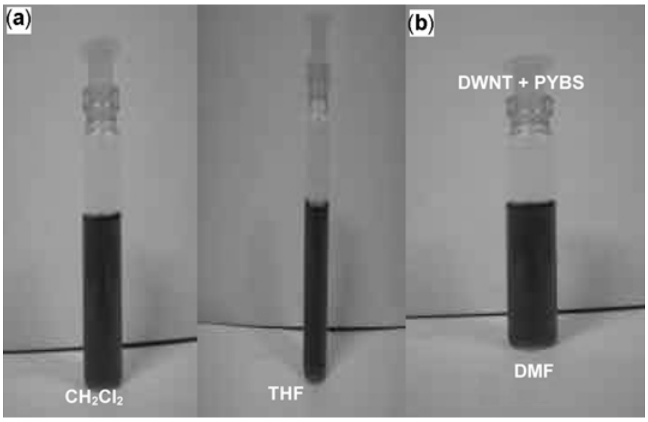

Figure 2. Photographs of vials containing the dispersions of DWNTs in various solvents: (**a**) amide-functionalized DWNTs, (**b**) PYBS functionalized DWNTs.

The D band shifts from 1310 to 1322 cm^{-1} after treatment with PYBS accompanied by an increase in intensity. PYBS-functionalized DWNTs are readily dispersible in dimethylformamide as shown in figure 2b. The nanotubes features are retained after functionalization is revealed by the TEM images in figure 3c. We notice debundling of the DWNTs after non-covalent functionalization with PYBS.

DWNTs could be non-covalently functionalized by using polyethylene glycol (PEG) as well. Figure 4a shows the Raman spectrum of DWNTs at various stages of the functionalization process. The inner wall RBM bands at 189 and 213 cm^{-1} of pure DWNTs are shifted to 186 and 211 cm^{-1} after treatment with PEG. The G band of pure DWNTs at 1575 cm^{-1} is shifted to 1581 cm^{-1} after treatment with PEG, while the D band shifts from 1310 to 1322 cm^{-1} accompanied by an increase in intensity. Thus, the RBM bands of inner tubes shift slightly on acid treatment and on further treatment with PEG. The intensities of the RBM bands of the outer tubes, however, get suppressed significantly on functionalization with PEG (figure 4a). PEG-functionalized DWNTs are dispersible in water as shown in figure 5a. The TEM image of the DWNTs after non-covalent functionalization by PEG is shown in figure 3d. The image shows debundling of the nanotubes.

We have also used polyoxyethylene(40)nonylphenyl ether (IGPAL) to non-covalently functionalize DWNTs. Figure 4b shows the RBM bands of DWNTs before and after functionalization with IGPAL. The RBM bands of the inner walls shift from 189 and 213 cm^{-1} to 185 and 208 cm^{-1} respectively with small changes in intensity after functionalization. The RBM band intensities of the outer walls get suppressed on functionalization. However, when compared to covalent functionalization, the outer wall RBM intensities are not as much affected. In the case of functionalized DWNTs, the external nanotubes were functionalized causing the modification of their outer walls. Hence the electronic structure and therefore the resonance conditions have been changed which determines the RBM intensities. Therefore, we observe a decrease in intensity of the bands below 170 cm^{-1}. There is no shift of the G band where as the D band shifts from 1310 to 1318 cm^{-1} with a slight increase in intensity after

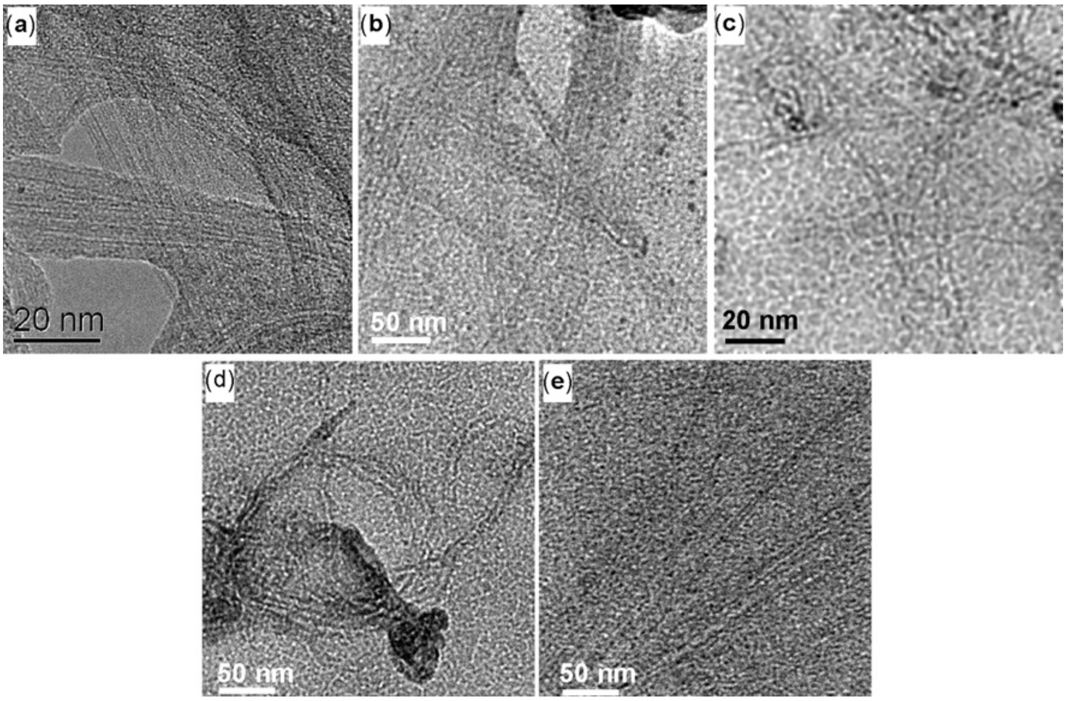

Figure 3. TEM images of DWNTs (**a**) pristine and (**b**) after covalent functionalization through amidation and (**c**, **d** and **e**) after non-covalent functionalization with PYBS, PEG and IGPAL respectively.

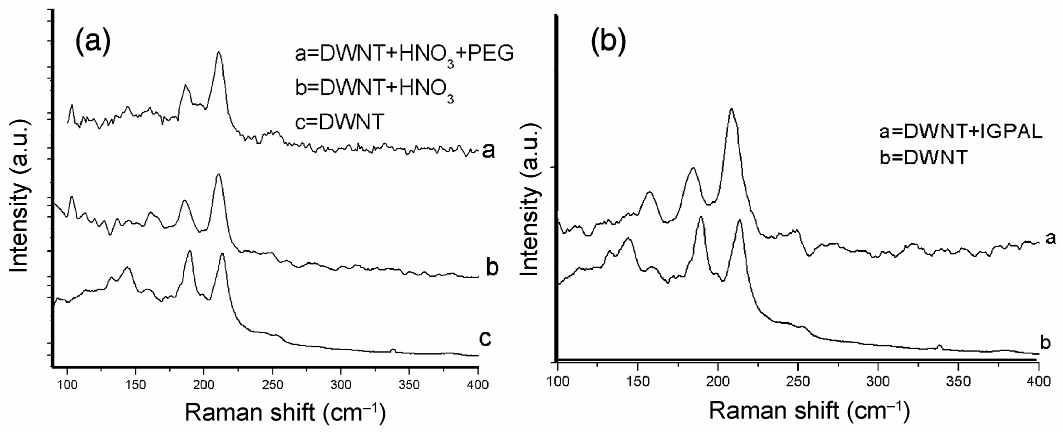

Figure 4. Raman spectra showing the RBM bands of pure and functionalized DWNTs at various stages: (**a**) with PEG and (**b**) with IGPAL.

functionalization. IGPAL-functionalized DWNTs are dispersible in water are shown in figure 5b. In figure 3e, we show the TEM images of DWNTs after functionalization with IGPAL. The dispersions were found to be stable even after keeping it for 7 days. From the TEM images, we notice significant debundling of the DWNTs after functionalization with IGPAL.

4. Conclusions

In conclusion, it has been possible to carry out both covalent and non-covalent functionalization of DWNTs to enable solubilization in various solvents. Covalent functionalization affects only the outer nanotube walls of DWNTs, leaving the inner tube intact as revealed by Raman spectroscopy. Solubili-

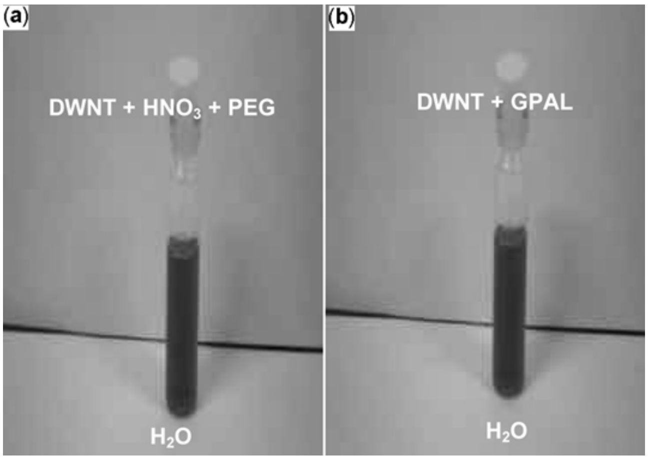

Figure 5. Photographs of vials containing the dispersions of functionalized DWNTs: (**a**) with PEG in water, (**b**) with IGPAL in water.

zation of DWNTs in non-polar solvents has been achieved through covalent as well as non-covalent functionalization. Non-covalent functionalization of DWNTs with surfactants helps to debundle the nanotubes. The nanotube structure is retained in the dispersions of DWNTs in both non-polar and aqueous media as revealed by Raman spectroscopy and transmission electron microscopy.

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