

Synthesis of dark brown single-walled carbon nanotubes and their characterization by HSQC-NMR

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Abstract. We report here a simple and effective approach to the covalent attachment of single-walled carbon nanotubes (SWCNTs) and azo compounds. The functionalized SWCNTs prepared (through a radical mechanism) have been used for a diazonium coupling reaction. The results showed that the chemical method used has improved the processability and solubility of the carbon nanotubes. The dark brown SWCNTs obtained which can produce a yellow colour in organic solvents were characterized by different spectroscopic analyses. Heteronuclear single quantum coherence spectra (¹³C-¹H HSQC) have been used to detect the carbon nanotube allylic protons. The morphology of the main product has been shown by scanning electron microscopy (SEM).

Keywords. Carbon nanotubes; heteronuclear single quantum coherence spectra; covalent attachment; azo compound.

1. Introduction

Carbon nanotubes (CNTs) which have been proved to be a novel type of nanostructure with remarkable chemical, electrical and mechanical properties,^{1,2} were first described by Iijima.³ In spite of the carbon nanotube applications in various fields of science and technology are found, their solubility is one of the remaining challenges. Consequently, a simple and high yield processing functionalization is needed to compensate this deficiency. There are two main approaches for the surface modification of CNTs. The first one is non-covalent functionalization⁴ and the second one is the molecules' covalent attachment to the carbon nanotube walls.⁵ Among these effective reactions, diazonium coupling to CNTs could be the most popular chemical route for the covalent functionalization of carbon nanotubes. On the other hand, azo compounds are one of the most important commercial and industrial compounds for paints, textiles, plastics and metal surface.^{6–9} Also, they play an important role in other practical uses such as biological reactions,¹⁰ optical storage technologies¹¹ and photo electronic effects.^{12–14} In the most cases, azo compounds should be in solid state, but their intrinsic tendency towards aggregation¹⁵ is a

major technical barrier which nanometerization process could resolve it.¹⁶ So in the present research, we used the covalent binding of diazonium salt to the functionalized single-walled carbon nanotubes (SWCNTs). It can produce coloured SWCNTs with high solubility and also improve the property of azo dyes or pigments. The main goal of this work is the use of NMR to specify the carbon nanotube protons.

2. Experimental

2.1 Materials

SWCNTs (Nanotimes Co., Chengdu, China, Purity >90%) which have purified as described in the literature,¹⁷ are known to have small diameter (~1 nm) and high purity (<0.1 at. % of residual metal). All the reagents and solvents were purchased from Merck and Aldrich.

2.2 Characterization

The resulting mixtures were sonicated in QS 10 ultrasonic bath. The electronic spectra of the products were investigated on an ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometer V570 Jasco. Fourier transform infrared (FTIR) spectra (in KBr pellets) were

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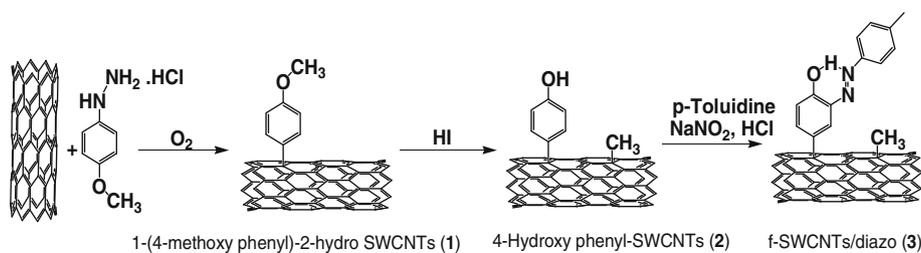


Figure 1. Schematic of chemical reactions on SWCNTs.

recorded on a Perkin-Elmer 1605 FTIR spectrometer. Raman spectra of the samples were recorded on an Amelga Thermo Nicolet Dispersive Raman spectrometer. Scanning electron microscopy (SEM) was performed on XL-30 Philips instrument. The nuclear magnetic resonance (NMR) spectrum was carried out on a Bruker AVANCE 500 MHz with a z-gradient triple resonance probe in ^{13}C - ^1H HSQC experiment. The spectral widths were 5000 Hz and 25000 Hz for the ^1H - and ^{13}C -dimensions, respectively. The number of collected complex points was 2048 for ^1H - dimension with a recycle delay of 5 s. The number of transients was 64, and 256 time increments were always recorded in ^{13}C -dimension. The $^1J_{\text{CH}}$ used was 140 Hz. The J -coupling evolution delay was set to 3.2 ms. DMSO- d_6 (δ_{C} 39.5; δ_{H} 3.35 ppm) and CDCl_3 (δ_{C} 77.4; δ_{H} 7.29 ppm) were used as solvents and TMS as an internal reference.

2.3 4-Hydroxy phenyl-SWCNTs (2) preparation

In a typical experiment (figure 1), purified SWCNTs were functionalized with 4-methoxy phenyl hydrazine hydrochloride in the presence of air oxygen through a free radical addition process¹⁸ to give 1-(4-methoxy phenyl)-2-hydro SWCNTs 1. The product obtained (10 mg, containing 1.67 mmol functional group) was sonicated with 30 ml dimethylformamide (DMF) for 30 min and was refluxed at 153°C in the presence of HI (211.2 mg, 1.65 mmol) for 3 h, after that, the mixture was filtered through a polytetrafluoroethylene (PTFE) membrane (pore size 0.2 μm). The final product was washed with methanol (100 ml) and 4-hydroxy phenyl-SWCNTs 2 collected (10 mg) were dried in vacuum at 80°C for 12 h.

2.4 f-SWCNTs/diazo compound (3) preparation

The resulting f-SWCNTs 2 (10 mg, containing 1.67 mmol phenoxyl functional group) were sonicated for 30 min with DMF (30 ml) to get a visually homogeneous suspension.

Fine powdered NaNO_2 (125.0 mg, 1.67 mmol) was added slowly and with stirring to the mixture of 4-methyl aniline (178.8 mg, 1.67 mmol), HCl (0.5 ml) and H_2O (3 ml). Temperature must be below 5°C. The solution was then added drop-wise to the primary suspension of f-SWCNTs 2 and Na_2CO_3 (212.0 mg, 2.0 mmol) in H_2O (5 ml). After stirring for 1 h, the nano azo product 3 was filtered and washed with H_2O until the filtrate become colourless. The f-SWCNTs/diazo 3 was dried in vacuum for 36 h before characterization (figure 1).

3. Results and discussion

3.1 Characterization of carbon nanotubes

3.1a UV-Vis-NIR spectra: The ultraviolet-visible-near infrared (UV-Vis-NIR) adsorption spectra of 4-hydroxy phenyl-SWCNTs 2 and f-SWCNTs/diazo 3 (0.2 mg/ml) have been shown in figure 2. Since we wanted to show the ability to produce colour of the main product, so we have gotten UV spectrum in visible region. While, the used van Hove singularities in the semiconducting nanotubes are centered at about 800–1400 nm and the band at about 500 nm for the metallic tubes can be less distinct and does not appear. Dark brown f-SWCNTs/diazo 3 is soluble in chloroform or other organic solvents and gives yellow liquor. It has a maximum absorption at 340 nm ($\log \epsilon = 2.30$) corresponding to the $\pi \rightarrow \pi^*$ transition of *trans*-azobenzene. Whereas, 4-hydroxy phenyl-SWCNTs 2 is not soluble in CHCl_3 and it has not shown any maximum absorption.

3.1b FTIR spectra: Fourier transform infrared (FTIR) spectroscopic analysis of 4-hydroxy phenyl-SWCNTs 2 and f-SWCNTs/diazo 3 confirms the presence of C–N (1027 cm^{-1}), N = N (1430 cm^{-1}), C = C (1641 cm^{-1}), aliphatic and aromatic C–H (2854–3000 cm^{-1}), and -OH (3427 cm^{-1}) functional groups at the surface of SWCNTs. In the case of 4-hydroxy phenyl-SWCNTs 2, some of the mentioned peaks were

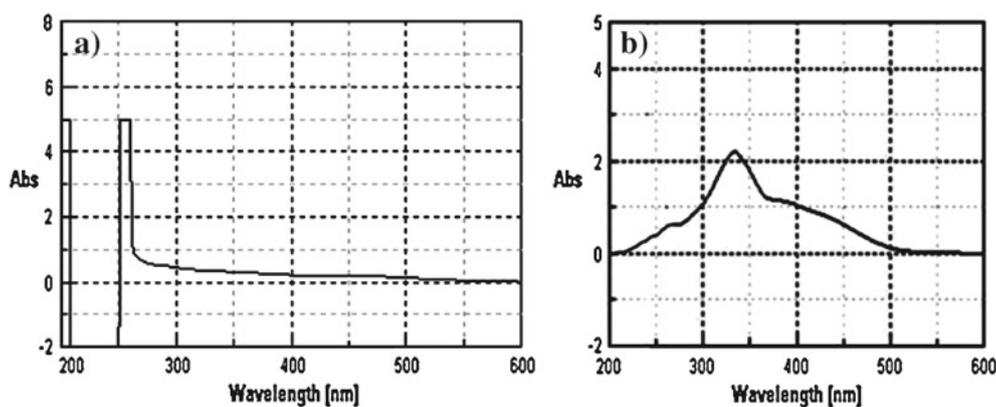


Figure 2. UV-Vis spectrum of (a) 4-Hydroxy phenyl-SWCNTs **2**, (b) f-SWCNTs/diazo **3**.

found in FTIR spectrum of it with lower intensity and a bit shift. Consequently, the characteristic bands of the final product **3** might overlap with the features of precursor **2** (figure S1).

3.1c Raman spectra: Raman spectroscopy has been extensively used to probe the structural and electronic properties of carbon nanotubes. The most important bands in Raman spectra of f-SWCNTs/diazo **3** are the strong G band at 1582 cm^{-1} which ascribed to the in-plane C–C stretching vibrational mode in graphite sheets and D band at around 1337 cm^{-1} is related to scattering from amorphous carbon and structural defects present in SWCNTs. In addition, a 2D-band occurs at 2663 cm^{-1} which is the second harmonic of D-band. The radial breathing modes (RBMs) about 280 cm^{-1} attributed to the collective breathing vibration of the entire SWCNTs, indicating little or no tube damage. Also, the high intensity of RBM in Raman spectrum of **3** reveals the nanotube diameters are below 2 nm (figure S2).¹⁹

Moreover, Raman bands of f-SWCNTs/diazo **3** show small frequency shift and large intensity changes in comparison with 4-hydroxy phenyl-SWCNTs **2**. It is evident that the covalent attachment of diazo compound to precursor **2** results in the appearance of Raman new bands for f-SWCNTs/diazo **3**. Down-shift of RBM mode for the main product **3** related to the decreased interaction between carbon nanotubes (debundling) through more functional groups on it. Also, the reduction of D/G ratio in primary 4-hydroxy phenyl-SWCNTs **2** confirmed the higher purity of it in comparison with f-SWCNTs/diazo **3**.

3.1d SEM images: Structural characterization of the pristine nanotubes and f-SWCNTs/diazo **3** was performed using scanning electron microscopy (SEM).

We present the images of pristine SWCNTs in figure 3a. They exhibit the microscopic fibre-like ropes which appear to be flexible and the fibre-like entities having typical diameters about 35 nanometers. As can be seen after functionalization (figure 3b), nanotubes are dispersed better than as-received SWCNTs and azo pigment clusters are attached to nanotube surfaces which leads to an increase of the intershell spacing as well.

3.1e ^{13}C - ^1H HSQC-NMR spectra: An essential and logical method in exploring the manifesting of covalent attachment would be nuclear magnetic resonance (NMR) spectra. So, the chemical structure of f-SWCNTs/diazo **3** was investigated by ^1H NMR, ^{13}C NMR and ^{13}C - ^1H HSQC analyses. As can be seen in table 1, the ^1H NMR spectrum of it in $\text{DMSO-}d_6$ has displayed a singlet at 10.97 ppm which is arising from hydroxyl proton with intramolecular H-bonding. The protons in toluene moiety were resonated at 7.89 and 7.38 ppm as doublets ($^3J \cong 8\text{ Hz}$). Also, the aromatic protons in phenolic ring have been appeared at 7.56 ppm as singlet, at 7.22 and 6.95 ppm as doublets ($^3J \cong 8\text{ Hz}$). The singlet proton at $\delta = 7.56\text{ ppm}$ shows the arrangement of diazo component. The most important characteristic signals in ^1H NMR of f-SWCNTs/diazo **3** are the allylic protons connecting to the nanotubes as a singlet at 2.52 ppm and two methyl groups connecting to the carbon nanotube side walls and benzene ring at 2.40 and 2.28 ppm.

The ^{13}C NMR spectrum of f-SWCNTs/diazo **3** in $\text{DMSO-}d_6$ (table 1) exhibited some peaks between 118 and 152 ppm readily recognized as arising from aromatic and olefinic carbons resonances. Also, methyl groups have been appeared at 21.04, 19.96 ppm, respectively. Nanotube allylic carbons were also observed being overlapping with the signals of solvent, but ^{13}C - ^1H HSQC spectroscopy (figure 4) shows their relation to the corresponding protons ($\delta\text{C}/\delta\text{H}$ 40.0/2.5 ppm).

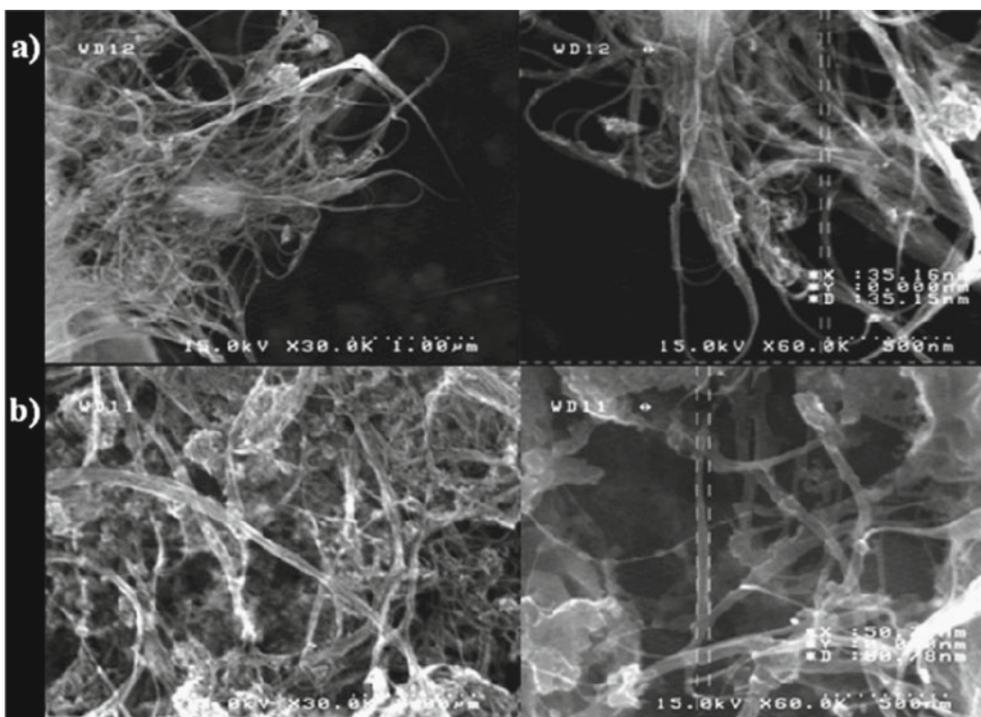
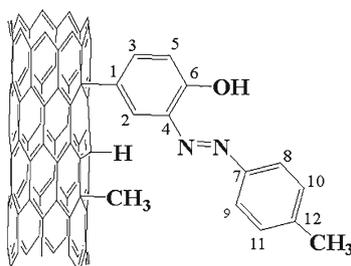


Figure 3. SEM image of (a) pristine nanotubes (b) f-SWCNTs/diazo 3.

Table 1. NMR chemical shifts (ppm) of f-SWCNTs/diazo **3** and ^{13}C - ^1H HSQC assignment.



	$^1\text{HNMR}$	$^1\text{HNMR}$	$^{13}\text{CNMR}$	$^{13}\text{CNMR}$	HSQC
C_1	–	–	137.79	137.40	–
C_2, H_2	7.56 s	7.76 s	123.13	133.18	123.1/7.6
C_3, H_3	6.95 d	6.95 d	117.89	118.20	117.9/6.9
C_4	–	–	152.13	151.22	–
C_5, H_5	7.22 d	7.17 d	134.10	134.28	134.1/7.2
C_6	–	–	141.44	142.55	–
C_7	–	–	149.46	149.18	–
$\text{C}_8, \text{H}_8\text{-C}_{11}, \text{H}_{11}$	7.89, 7.38 d	7.79, 7.34 d	129.94, 122.53	130.42, 122.55	129.9/7.4 122.5/7.9
C_{12}	–	–	128.57	129.55	–
CH_3	2.40 s	2.41 s	21.04	21.92	21.0/2.4
OH	10.97	12.77	–	–	–
SWCNTs- CH_3	2.28 s	2.38 s	19.96	20.72	19.9/2.3
SWCNTs- CH	2.52 s	2.98, 2.91 s	–	39.42	40.0/2.5
SWCNTs- $\text{C}_{\text{sp}3}$	–	–	–	38.12	–

d: doublet; s: singlet

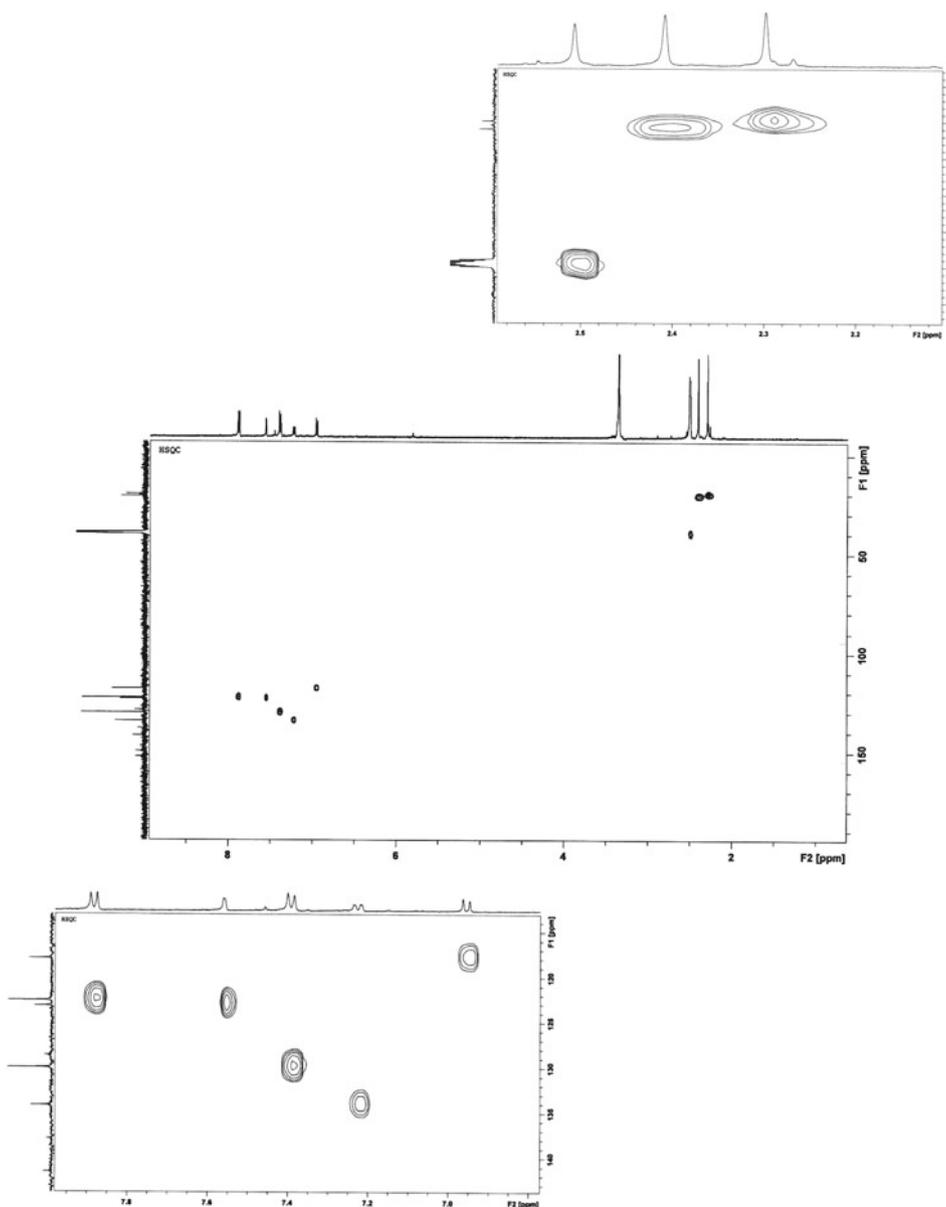


Figure 4. ^{13}C - ^1H HSQC-NMR spectrum of f-SWCNTs/diazo 3.

The ^{13}C - ^1H HSQC spectrum which has been presented in figure 4 has a projection onto the F2 axis which corresponds to the normal ^1H spectra and the projection onto the F1 axis corresponds to a normal ^{13}C spectrum, but with the quaternary carbons missing. It shows the region δ_c/δ_H 0–200/2–8 ppm. The existence of methyl protons which have attached to the carbon nanotube walls was evident by this technique (δ_c/δ_H 19.9–21.0/2.1–2.3 ppm). Also, the remaining protons which are related to the region of aromatic carbons (δ_c/δ_H 118.0–134.1/6.9–7.9 ppm) were specified in table 1.

Furthermore, the ^1H NMR and ^{13}C NMR of final product 3 in CDCl_3 confirm the allylic protons and carbons of SWCNTs. As reported in table 1, the same signals

were characterized by these spectrums with a bit shift. But the sp^3 carbons on the nanotubes have appeared better than before (38.12 and 39.42 ppm).

4. Conclusion

The chemical functionalization of carbon nanotubes is an attractive target as it can improve the unique properties of CNTs to be coupled to other types of materials. In spite of extensive investigation on the non-covalent functionalization of multi-walled carbon nanotubes (MWCNTs), the reported works about covalent functionalization of single-walled carbon nanotubes is still scant. So, we focus on the covalent attachment of diazo

functional group to the surfaces of single-walled carbon nanotubes through a simple approach. In conclusion, we could prepare dark brown SWCNTs with the ability to produce colour. The products obtained were characterized by UV-vis-NIR, FTIR, Raman and SEM technique and the chemical shift of the allylic protons connecting to the side walls of carbon nanotubes have been assigned by ^{13}C - ^1H HSQC-NMR spectroscopy for the first time.

Supporting material

Supplementary material given as figures S1–S2 can be seen online www.ias.ac.in/chemsci.

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