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Synthesis of water-soluble single-walled nanotubes by functionalization via esterification

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ABSTRACT

Water soluble compounds were attached to single-walled carbon nanotubes (SWNTs) to form water-soluble nano dyes. functionalized SWNTs were then characterized by Fourier Transform Infrared spectroscopy (FT-IR), Raman spectroscopy, scanning electron microscopy (SEM) and UV analysis. The product can be dissolved in water and High-resolution transmission electron microscope images showed that the SWNTs were efficiently functionalized, thus the p-stacking interaction between aromatic rings and COOH of SWNTs was considered responsible for the high solubility and High transmission electron in singlewall nanotubes.

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KEYWORDS

Functionalized CNTs;
Singlewalled carbon
nanotubes;
Water soluble compounds.

INTRODUCTION

The discovery of carbon nanotubes (CN) and the prospect of developing novel carbon-based nanomaterials has excited worldwide interest among researchers^[1, 2]. Single-walled carbon nanotubes (SWNTs) have drawn much attention because of their unique structural, electronic, mechanical and optical properties and the potential applications in nanotechnologies^[3]. Organic dyes and pigmentes have a group as their chromophore such as N=N, N=O or SO₃H^[4]. The synthesis of water-soluble carbon nanotubes is an important topic because such materials have potential applications in water base systems such as polymers^[5-15] crown ethers^[16] glucosamines^[17] and diazo dyes^[18]. Like halogenation and nitration, sulfonation is of the greatest importance in dye manufac-

ture. Most of the water soluble dyes owe their solubility to the presence of sulfonic acid groups. In this paper we present a simple route for sulfonation of organic compounds^[19], and then the products were successfully attached to SWNT-COOH via esterification method.

EXPERIMENTAL

All reagents and solvents were obtained from Merck Chemical Inc. and SWNT-COOH (90% purity, 1-2 nm) were purchased and used as received. The FT-IR spectrum was recorded using KBr tablets on a Nexus 870 FT-IR spectrometer (Thermo Nicolet, Madison, WI). FT-Raman spectra were recorded on 960 ES spectrometer (Thermo Nicolet), UV-visible spectra were recorded on a UV-Visible spec-trometer

(GBC Cintra 20, Victoria, Australia), ^1H NMR spectrum was recorded on Bruker DRX-300 Avance spectrometer at solution in CDCl_3 using TMS as internal standard. SEM was used to study the morphology of the SWNTs. SEM measurement was carried out on the XL30 electron microscope (Philips, Amsterdam, Netherlands).

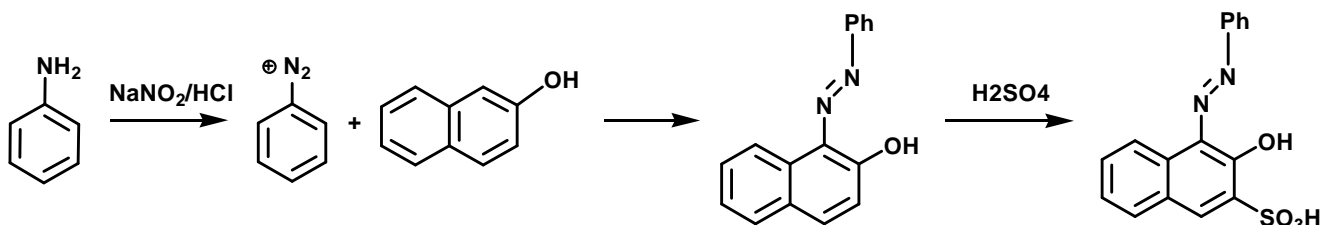


Figure 1 : Synthesis route of (E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid

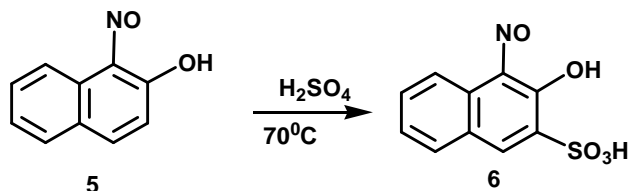


Figure 2 : Synthesis route of 3-hydroxyl-4-nitrosonaphthalene-2-sulfonic acid

the mixture filtered and washed with alcohol to produce compound 5^[19,20].

Redish: Orange, power: (85%), mp=120-122°C (decomp), IR(KBr, cm^{-1}), 3400 broad (OH, SO_3H), 2820 (C-H), 1571-1390 (NO_2), 1623 (N=N), 1180 (S=O), 740 (S-O). ^1H NMR(300MHz, CDCl_3) δ : 6.44-8.96 (m, H Aromatic), 9.12(1H, s, OH), 10.83(1H, s, OH), 13.16(1H, s, OH).

Preparation of 3-hydroxy-4-nitrosonaphthalene-2-sulfonic acid

A mixture of 1.5 gr of α -nitroso- β -naphthol^[21] and 1.5 mL of concentrated sulfuric acid heated at 70°C for three hours. Boiling water bath replaced by an ice bath. Then the mixture filtered and washed with water. The product was obtained as brown powder (62%), mp =225-227°C. IR (KBr) 3200 (SO_3H), 3174 (OH), 1644 (C=C), 1480 (NO), 1214 (S=O) cm^{-1} . ^1H NMR (500.1 MHz, CDCl_3) δ : 7.4-8.1(m, Ar), 8.73, 8.70 (2H, 2 OH).

Preparation of SWNT-(E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid and SWNT-3-hydroxy-4-nitrosonaphthalene-2-sulfonic acid

30 mg of SWNT-COOH were sonicated in 30

Preparation of (E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid

Azo salt 2 was prepared by adding HCl / NaNO_2 to aniline 1 at 0°C. This salt was coupled to β -naphthol 3 and produced azo compound 4. The product and concentrated sulfuric acid heated at 70°C for three hours. Boiling water bath replaced by an ice bath. Then

mL of N,N-dimethyl formamide (DMF) for 35 minutes to give a homogeneous suspension. Compounds 4 and 6 were added to the SWNT suspension at 0°C. Any mixture was stirred at 0°C for two hours and then triethylamine and HCl were added to the mixture. The reaction mixture was kept at room temperature for 7 days (Figure 3). Finally, the final products 7 and 8 were filtered and washed thoroughly with DMF and acetone. Subsequently, the black solids were vacuum-dried at room temperature for 2 hours.

RESULTS AND DISCUSSION

Figure 2 shows the FT-IR spectra of SWNT-COOH and the modified SWNTs. In spectrum 1, the band at around 1637 cm^{-1} corresponds to the stretching mode of the C=C double bond that forms the framework of the carbon nanotube sidewall^[22]. The peak at 1715 and 3442 cm^{-1} apparently corresponds to the stretching modes of the carboxylic acid groups^[23]. The two bands at around 2800–2900 cm^{-1} which are seen in tow spectrum are attributed to the CH stretching of SWNT-COOH defects. In spectrum 2, the peak at 1739 cm^{-1} can be attributed to the C=O stretch of the ester. The peaks observed at 1557 and 1353 cm^{-1} are corresponds to the NO_2 group, while the peak at 1280 cm^{-1} corresponds to the S=O in SO_3H group, and the peak at 1118 cm^{-1} arises from the C-O stretch of the ester group. The band at around 1700 cm^{-1} apparently corresponds to the stretching modes of N=N group^[24]. Many of these vibrational modes have been

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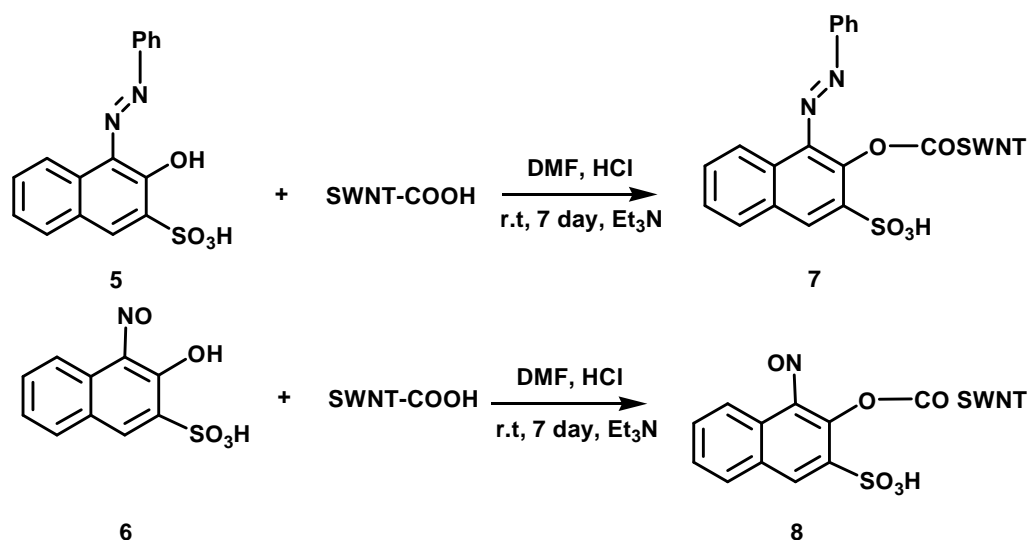


Figure 3 : Synthesis route of modified SWNT-COOH via esterification method

reported previously for functionalized SWCNTs^[25]. In spectrum 3, the peak at 3363 cm^{-1} can be assigned to CH stretching of aromatic rings, carbonyl peak in the spectrum 3 shift to 1716 cm^{-1} is a result of ester linkage formation. The band at around 1111 cm^{-1} corresponds to the C-O stretching mode in esters, the peak at 1436 cm^{-1} corresponds to the N=O, the peak at 1183 cm^{-1} corresponds to the S=O in SO_3H group. The peaks at 602 and 800 cm^{-1} are bands originating from the aromatic rings^[26].

Raman spectra offer useful information concerning the slightly structural changes of SWNTs, especially the changes owing to significant sidewall modification. As can be seen in Figure 4, the characteristic peaks of SWNT tangential modes, namely the diameter dependent radial breathing mode (R band) at 210 cm^{-1} depending on the diameter of nanotubes, the D band at around 1330 cm^{-1} and the G band at around 1500 cm^{-1} slightly changed. In this research for SWNT-(E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid and SWNT-3-hydroxy-4-nitrosophthalene-2-sulfonic acid, we observed the radial breathing modes were suppressed and shifted to 214 and 219 cm^{-1} by the introduction of the SWNT-(E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid and SWNT-3-hydroxy-4-nitrosophthalene-2-sulfonic acid respectively and an increase in the ratio of intensities ID/IG, from 0.65 to 1.12 and from 0.65 to 1 respectively. This indicates an increased disorder of the graphitic structure of the modified nanotubes, which shows that the nanotubes were modified^[27-34].

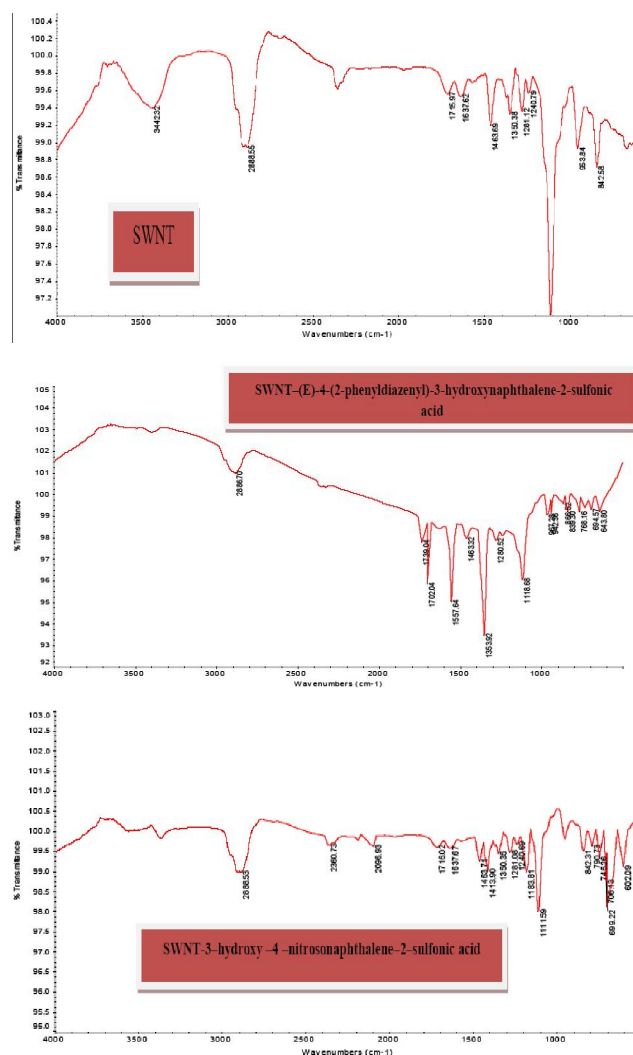


Figure 4 : IR spectra for SWNT and SWNT-(E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid and SWNT-3-hydroxy-4-nitrosophthalene-2-sulfonic acid

More direct evidence for the functionalization of nanotubes is manifested by SEM images^[35]. In Figure 4, SEM images of A (SWNT-COOH) and B (SWNT-(E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid) and C (SWNT-3-hydroxy-4-nitronaphthalene-2-sulfonic acid) are shown. It indicates that the "A" has a smooth surface. The changes in the morphology for "B" and "C" are remarkable (Figure 5). It seems that the diameters of "B" and "C" are slightly increased in comparison to "A".

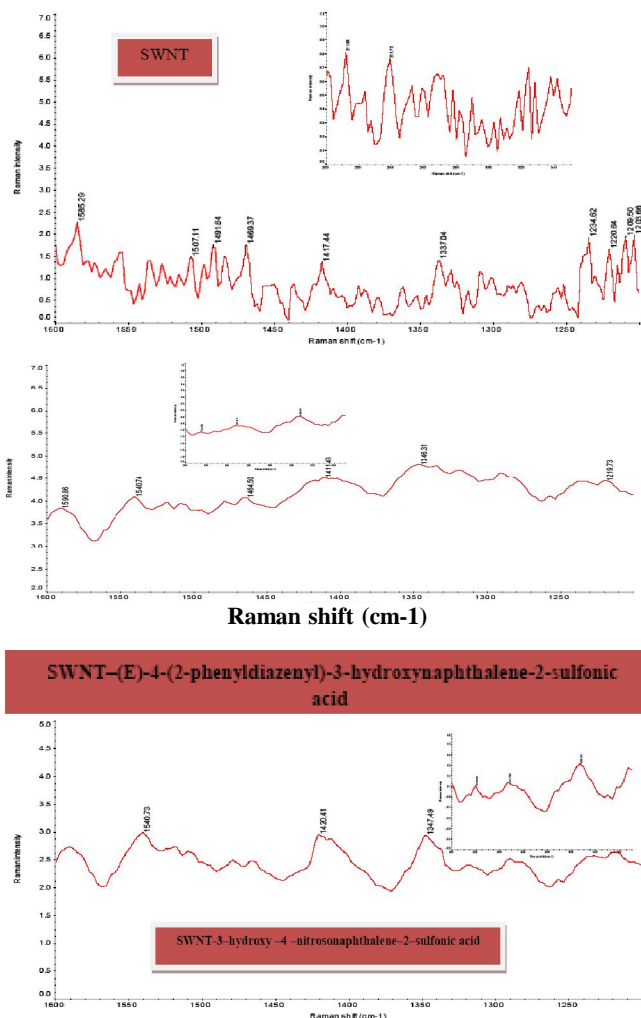


Figure 5 : Raman spectra for SWNT and SWNT-(E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid and SWNT-3-hydroxy-4-nitronaphthalene-2-sulfonic acid.

The functionalization of SWNT can be confirmed by the UV-visible spectra shown in Figure 6, in which the curve a (SWNT-COOH) and curve b (SWNT-(E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid) and curve c (SWNT-3-hydroxy-4-nitronaphthalene-2-sulfonic acid) were compared to

show the changes in characteristic signals.

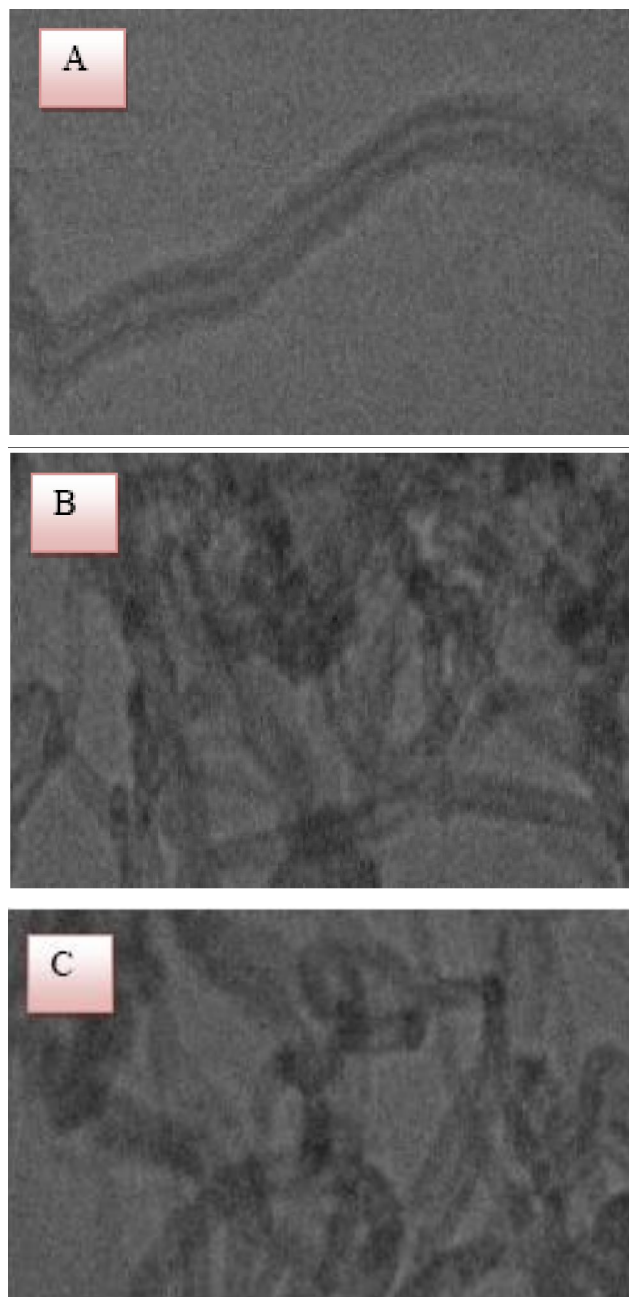


Figure 6 : TEM images of (A) and (B) and (C)

UV spectra of SWNT-COOH (A) and SWCNT-(E)-4-(2-phenyldiazenyl)-3-hydroxynaphthalene-2-sulfonic acid (B) and SWNT-3-hydroxy-4-nitronaphthalene-2-sulfonic acid (C) were recorded as 1 mg in 1000 cc H₂O, λ_{\max} and A (Absorbance) summarized in Table 1. The increase of λ_{\max} in B and C were assigned to transmission electron of $\pi \rightarrow \pi^*$ in N=N and N=O in water soluble pigments.

The chemistry of nanotubes offers considerable

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TABLE 1 : λ_{\max} and A of SWNT-COOH (A) and SWCNT - (E) -4 - (2 - phenyldiazenyl) - 3 - hydroxynaphthalene -2 - sulfonic acid (B) and SWNT - 3 -hydroxy-4-nitrosophthalene-2-sulfonic acid (C).

Name	λ_{\max} (nm)	A
A	202	0.154
B	432	0.056
C	235	0.252

TABLE 2 : Yields of functionalized and de functionalized samples of SWNT-COOH (A) and SWCNT- (E) -4 -(2-phenyldiazenyl) -3-hydroxynaphthalene -2-sulfonic acid (B) and SWNT -3-hydroxy -4 -nitrosophthalene -2-sulfonic acid (C).

Samples	Yields of functionalized samples	Yields of defunctionalized samples
A	5 mg	4.5 mg
B	5 mg	4.8 mg

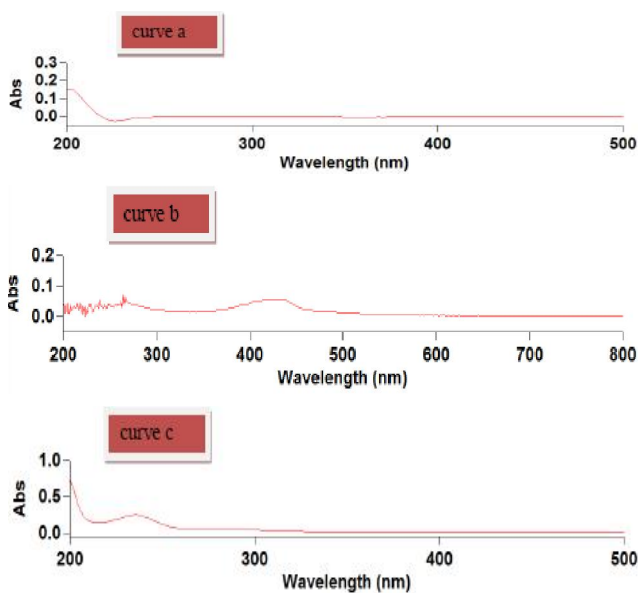


Figure7 : Ultra Violet images of (A) and (B) and (C)



Figure 8 : The dispersion of modified-SWNTs (before and after sonication) in deionised water after standing for 2 months.

scope for development of functional materials, structures and devices based on SWNTs. A detailed methodology for the modification and functionalization of single walled carbon nanotube via esterification has been presented. We have introduced water soluble pigments on the surface of nanotubes. The functionalized SWNTs was demonstrated by SEM images, FT-IR, Raman spectroscopy and UV analysis, the results show successful functional groups.

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REFERENCES

- [1] S.Iijima, Helical; Microtubules of graphitic carbon, *Nature*, **56**, 354 (1991).
- [2] (a) P.M.Ajayan, O.Z.Zhou; *Top.Appl.Phys.*, **80**, 391 (2001); (b) P.M.Ajayan; *Chem.Rev.*, **99**, 1787 (1999).
- [3] M.S.Dresselhaus, G.Dresselhaus, P.Avouris; *Carbon Nanotubes Synthesis, Structure, Properties, and Applications*, New York Springer-Verlag (2001).
- [4] A.T.Rowland, Allen K.Clark, Carl T.Wigal, Charles E.Bell Jr., Douglass F.Taber, Frederick A.Bettelheim, Jan William Simek, Jerry Manion, Joe Jeffers, Joseph M.Landesberg, Joseph W.LeFevre, L.G.Wade Jr., Louis J.Liotta, Moses Lee, Ronald J.Wikholm, William M.Loffredo; *Organic Chemistry Laboratory Manual*, Susquehanna University Thomson Learning, Ohio, (2003).
- [5] J.E.Riggs, Z.X.Guo, D.L.Carroll, Y.P.Sun; *Am. Chem.Soc.*, **122**, 5879-5880 (2000).
- [6] J.E.Riggs, D.B.Walker, D.L.Carroll, Y.P.Sun; *Phys. Chem.B*, **104**, 7071-7076 (2000).
- [7] K.Fu, W.Huang, Y.Lin, L. A. Riddle, D.L. Carroll; Y.P. Sun; *Nano Lett.*, **1**, 439-441 (2001)
- [8] Y.P.Sun, W.Huang, Y.Lin, Y.Kefu, A.Kitaygorodskiy, L.A.Riddle, Y.Yu, D.L.Carroll; *Chem.Mater*, **13**, 2864-2869 (2001).
- [9] R.Czerw, Z.Guo, P.M.Ajayan, Y.P.Sun, D.L.Carroll; *Nano Lett.*, **1**, 423-427 (2001).
- [10] M.Sano, A.Kamino, J.Okamura, S.Shinkai; *Langmuir* **17**, 5125-5128 (2001).
- [11] W.Huang, Y.Lin, S.Taylor, J.Gaillard, A.M.Rao, Y.P.Sun; *Nano Lett.*, **2**, 231-234 (2002).

- [12] D.E.Hill, Y.Lin, A.M.Rao, L.F.Allard, Y.P.Sun; *Macromolecules*, **35**, 9466-9471 (2002).
- [13] Y.Lin, A.M.Rao, B.Sadanadan, E.A.Kenik, Y.P.Sun; *Phys.Chem.B*, **106**, 1294-1298 (2002).
- [14] L.Huang, Y.Huang, J.Liang, X.Wan, Y.Chen; *Nano Res.*, **4(7)**, 675-684 (2011).
- [15] M.G.C.Kahn, S.Banerjee, S.S.Wong; *Nano Lett.*, **2**, 1215-1218 (2002).
- [16] F.Pompeo, D.E.Resasco; *Nano Lett.*, **2**, 369-373 (2002).
- [17] M.Hazani, R.Naaman, F.Hennrich, M.M.Kappes; *Nano Lett.*, **3**, 153-155 (2003).
- [18] H.Chengguo, Ch.Zilin, Sh.Aiguo, Sh.Xincheng, L.Jie, H.Shengshui; *Carbon*, **44**, 428-434 (2004).
- [19] H.Fieser, L.Blangey; 'Fundamental Processes of Dye Chemistry', Inter Science Publishers, Inc., New York, 126-128 (1931).
- [20] I.Bridgeman, A.T.Peters; *J.Soc.Dyers Colourists*, **86**, 519-524 (1970).
- [21] C.Y.Hu, Y.J.Xu, S.W.Duo, R.F.Zhang, M.S.Li; *Chin Chem Soc.*, **56**, 234-238 (2009).
- [22] M.Holzinger, O.Vostrowsky, A.Hirsch, F.Hennrich, M.Kappes, R.Weiss; *Angew.Chem., Int.Ed.Engl.*, (2001).
- [23] Y.P.Sun, K.Fu, Y.Lin, W.Huang; *Acc.Chem.Res.*, **35**, 1096 (2002).
- [24] K.J.Morgan; *J.Chem.Soc.*, 2151, (1961).
- [25] M.A.Hamon, H.Hui, P.Bhowmik, H.M.E.Itkis, R.C.Haddon; *Appl.Phys.A*, **74**, 33-338 (2004).
- [26] E.A.Zaragoza Contreras, E.D.Lozano-Rodriguez, M.Roman-Aguirre, W.Antunez-Flores, C.A.Hernandez-Escobar, G.Sergio, A.Aguilar; *Elguezabal.Micron*, **40**, 621 (2009).
- [27] A.Hirsch; *Angew.Chem.Int.Ed.Engl.*, **41**, 853 (2002).
- [28] M.A.Hamon, J.Chen, H.Hu; *Adv.Mater.*, **11**, 8340-8340 (1999).
- [29] M.A.Hamon, H.Hu, P.Bhowmik; *Chem.Phys.Lett.*, 347-348 (2001).
- [30] A.Jorio, R.Saito, G.Dresselhaus, M.S.Dresselhaus; *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences*, **362**, 2311-2336 (2004).
- [31] A.M.Rao, E.Richter, S.Bandow, B.Chase, P.C.Eklund, K.A.Williams, S.Fang, K.R.Subbaswamy, M.Menon, A.Thess, R.E.Smalley, G.Dresselhaus, M.S.Dresselhaus; *Science*, **275** 187-191 (1997).
- [32] M.S.Dresselhaus, G.Dresselhaus, R.Saito, A.Jorio; *Physics Reports-Review Section of Physics Letters*, **409**, 47-99 (2005).
- [33] C.Thomsen, S.Reich, J.Maultzsch; *Physical and Engineering Sciences*, **362**, 2337-2359 (2004).
- [34] T.Nakamura, M.Ishihara, T.Ohana et al.; *Diam . Relat.Mater*, **13**, 1971-1974 (2004).
- [35] D.Mattia; *Templated Growth and Characterization of Carbon Nanotubes for Nanofluidic Applications*, PhD Thesis, Drexel University, 49 (2007).