Reversible functionalization of multi-walled carbon nanotubes with organic dyes

W. Zhang^{*} and S. R. P. Silva

Nanoelectronics Centre, Advanced Technology Institute, University of Surrey,
Guildford, Surrey GU2 7XH, United Kingdom

Multi-walled carbon nanotubes are dispersed in water *via* the formation of adducts with dyes, where the process may be monitored by the visual observation of colour variations of dye solutions. Atomic force microscopy images corroborate evidence for attachment of dyes on nanotubes. Laser Raman and Fourier transform infrared spectroscopies suggest intimate electronic interactions between nanotubes and dyes. By thin layer chromatography technique, dyes are successfully exfoliated from nanotubes, showing the reversible nature of the process.

Keywords: Carbon nanotubes; Raman spectroscopy; Infrared (IR) spectroscopy; Atomic force microscopy (AFM); Thin layer chromatography (TLC)

Carbon nanotubes (CNTs) exhibit unique structural, mechanical, and electrical properties and are intensely studied for possible use in many fields. As commonly produced, CNTs consist of many different diameters and chiralities and contain impurities. Most purification and separation methods for CNTs require CNTs to be

^{*} Corresponding author. E-mail: zhangweileeds@hotmail.com

processed as a liquid dispersion. However, their low solubility in water/solvent has significantly hindered this process [1]. Chemical oxidation of CNTs, using $\text{H}_2\text{SO}_4/\text{HNO}_3$ [2], $\text{K}_2\text{Cr}_2\text{O}_7$ [3], CO_2 gas [4], microwave-excited Ar/O_2 surface-wave plasma treatment[5], can remarkably enhance their solubility. In addition to this, covalent functionalization of CNTs with fluorine[6], chlorine and bromine[7], alkane[8], diazonium salt [9] can also improve their solubility. Unavoidably, this kind of modification opens either the ends or the sidewalls of nanotubes, disrupting the π -electron system and impairing the tubes' electronic properties [10]. Significant efforts have also been devoted to using organic solvents to stabilize CNT dispersions and it was found that amide solvents (*e.g.* *N,N*-dimethylformamide, *N*-methylpyrrolidone) [11] and dichlorobenzene [12] are more appropriate media. As these organic solvents are incompatible with living organisms, these methods often exclude themselves for consideration in biochemistry and biomedical engineering. Non-covalent functionalization of CNTs with surfactants [13], polymers [14], DNA [15], peptides [16] and starch [17], γ -cyclodextrin [18], can effectively disperse CNTs in aqueous medium. However, the removal of attached large moieties after processing is problematic. A technique that can be adopted for water solubilization of CNTs in a reversible manner is still highly desirable. In this letter, organic dyes were applied to disperse CNTs into water by the generation of CNT/dye adducts, and subsequently these adducts were separated by thin layer chromatography. This is a mild, convenient and economical method and has the benefit of the whole procedure being qualitatively monitored by the observation of visual appearance.

To obtain multi-walled carbon nanotube (MWCNT)/dye adduct dispersions, the mixture of dye (10 mg, Kemtex Education Supplies, UK) and MWCNTs (10 mg, inner diameter: 5-10 nm, outer diameter: 10-20 nm, length: 0.5-200 μm , Sigma-Aldrich, UK) in 100 cm^3 de-ionized water was sonicated in QS 10 ultrasonic bath (Ultrawave Ltd., UK) for 40 mins. After vacuum filtration, the filtrate was collected.

Fig. 1 witnesses the colour differences between dye solutions (a, c, e, g) and MWCNT/dye adduct dispersions (b, d, f, h). Compared with pure dye solutions, the involvement of MWCNTs incurs a colour change. Two factors may be invoked to explain this phenomenon. On one hand, MWCNTs can absorb a certain frequency of electromagnetic waves as a black species; on the other hand, as hydrophobic particles, MWCNTs can change the optical scattering properties of dye solutions. Both can affect light-solution interactions and consequently create a variation in visible light. When illuminated with focused laser light in a darkened room, dye solutions and MWCNT/dye adduct counterparts exhibit distinctions, as shown in Fig. 1. A clearly visible light path can be observed when the laser travels through MWCNT/dye adduct 'solution', *i.e.* Tyndall phenomena, whereas pure dye solutions show up as 'transparent'. As the Tyndall effect suggests the existence of a colloidal system, more precisely speaking, MWCNTs are dispersed rather than dissolved in water. Aside from the colour change of dye solutions, this also indicates the dispersion of MWCNTs in dye solutions.

Hereafter, direct yellow (DY) was used as a sample dye to demonstrate our work. To further envisage MWCNT/dye adducts, atomic force microscopy (AFM, a Veeco model D 3100) observations were carried out. As Fig. 2a shows, the functionalization of

MWCNTs with dyes exhibits a considerable debundling effect and discrete nanotubes can be observed. 3-Dimensional images (Fig. 2b) display that dye molecules are indeed attached on to the nanotubes' surface, visible as light areas covering the nanotube and a rough tube surface.

The typical Raman spectra (recorded on a Renishaw System 2000, UK) of MWCNTs and MWCNT/dye adducts were shown in Figure 3d. The spectrum of MWCNTs shows two characteristic bands: the G-mode ($\sim 1590\text{ cm}^{-1}$) and D-mode ($\sim 1350\text{ cm}^{-1}$). For MWCNT/dye adducts, these two characteristic bands are also present, indicating the existence of MWCNTs. In the meantime, a new band emerges at around 1400 cm^{-1} , which suggests the intimate interactions between MWCNTs and dye molecules.

Interestingly, the dye molecule (DY) contains two different sorts of carbonyl groups ($>\text{C}=\text{O}$), namely one in carboxylic acid (sodium salt) and the other in the amide group. As the stretching frequencies of these two carbonyl groups are quite close to each other, appearing at 1615 cm^{-1} and 1638 cm^{-1} ($\Delta\nu\ 23\text{cm}^{-1}$, see Fig.3c), it is hard to identify these infrared signals. In order to assign these two peaks to the corresponding carbonyl groups, the commercial dye powder was dissolved in water ($pH\ 7.5$), and parts of this solution was taken out and acidified with diluted hydrochloric acid to $pH\ 1.5$, and then both solutions were applied on the surface of KBr pellet and analyzed with the Fourier transform infrared (FTIR) spectroscopy (a Nicolet 460 FT-IR spectrometer, US). The spectra of dye in acid form show strong signals at 1662 cm^{-1} and 1638 cm^{-1} . Obviously, after acidification, the peak emerging at 1638 cm^{-1} remains at the same frequency, and the peak present at 1615 cm^{-1} shifts to 1662 cm^{-1} ($\Delta\nu\ 47\text{cm}^{-1}$). Therefore, absorption

peaks at 1615 cm^{-1} and 1638 cm^{-1} are assigned to carboxylic acid (salt form) and amide group, respectively. This is because, when acidified, the carboxylate sodium salt ($-\text{COONa}$) is converted to its 'weak' acid form ($-\text{COOH}$). When in salt form, hydroxyl oxygen is negatively charged, and thus holds a higher propensity to offer electrons and renders the conjugate interaction with the π -bond in carbonyl group. As a result, a much stronger p - π conjugate system is generated among O-C-O, and the negative charge is delocalized. This, in turn, diminishes the characteristic of the double bond ($>\text{C}=\text{O}$) and force constant, shifting the infrared signal to lower frequency. In the meantime, the acidification does not dramatically affect the chemical environment of the amide group and its infrared signal remains at the same position. In addition, comparing the FTIR spectra of dye (salt form) and MWCNT/dye adduct, it can be found that after functionalization the relative peak intensity of two carbonyl groups is substantially changed. This indicates either the amide or the carboxylic acid group interacts with nanotubes, although it is still hard to ascertain which one it is. The interactions with nanotubes change the chemical environment of the carbonyl group and affect the dipole moment, giving rise to the variation in absorption intensity.

Thin layer chromatography (TLC) is a simple, quick, and inexpensive technique that is widely used in organic chemistry to separate mixtures. Here, we borrow this technique to de-functionalize MWCNTs, *i.e.*, exfoliate dye molecules from nanotubes. The silica gel coated onto aluminium (Alugram®SilG/UV254, Germany) functions as the stationary phase. Solvent (mobile phase) consists of isopropanol and deionized water (1:1 v/v). As the solvent begins to soak up the plate, it first dissolves dye molecules due to the strong attraction between dye molecules and the solvent. When the mobile phase

flows through the stationary phase, dye molecules present will then tend to get carried up the chromatography plate as the solvent continues to move upwards. In contrast, nanotube exhibits very limited, if any, solubility in the solvent and sticks firmly to the stationary phase *via* hydrogen bonding and van der Waal force. Because different analytes (dye molecules and MWCNTs) ascend the TLC plate at different rates, separation is achieved and can be directly visualized as different coloured spots, diagrammatically shown in Figure 3b, wherein the yellow spots represent dyes and the black spots are nanotubes. It is noticeable that the yellow spots are always accompanied by short ‘tails’. This proposes not only that dye molecules are attached on nanotubes, but also the peeling off of dye molecules from nanotubes is a dynamic process. There is a constant movement of dye molecules between being adsorbed by nanotubes and pulling back into the solvent. There is no doubt that dye molecules can only travel up the plate during the time that they are dissolved in the solvent. While they are adsorbed by nanotubes, they are temporarily stopped - the solvent is moving on without them. Because of this slightly delayed travel of some dye molecules, tails are present in the chromatogram.

To further confirm the exfoliation of dye molecules from nanotubes, de-functionalized nanotubes were characterized by Raman spectroscopy, shown in Fig. 3d. It is evident that the generation of MWCNT/dye adduct results in the appearance of a new band (at around 1400 cm^{-1}), stemming from the electronic interactions between nanotubes and dye molecules. After de-functionalization, the newly emerging band in MWCNT/dye adduct disappears. This result further corroborates the separation of two species and the ‘recovery’ of nanotubes. The released dye was analyzed by FTIR, see Fig. 3c. In

contrast to the pristine dye (salt form), it seems the difference in stretching vibration frequency of two carbonyl groups (amide and carboxylic acid group) diminishes and only one broad peak can be observed. This may be related with the occurrence of intermolecular hydrogen bondings between dye molecules and active hydrogen and oxygen atoms present on silica surfaces. The formation of hydrogen bondings between carbonyl groups and active hydrogens in silica ($>\text{C}=\text{O}\cdots\text{H}-\text{O}-\text{Si}-$) widens the discrete absorption bands of carbonyl groups, and as these two characteristic frequencies are close to each other, band overlapping may be incurred and visualization of individual peaks become impossible. Another striking feature in FTIR spectra of the de-functionalized dye is the stretching signals of active hydrogens in hydroxyl and amine groups are blurred as well. This also suggests the enhancement of intermolecular hydrogen bondings ($-\text{Si}-\text{O}\cdots\text{H}-\text{dye}$), as the occurrence of hydrogen bondings widens not only the infrared band of the Lewis base but also the Lewis acid.

In summary, owing to the chemical structure characteristics of organic dyes, pristine MWCNTs can be dispersed in water by the generation of adducts with individual nanotubes surrounded by dye molecules. By TLC technique, dye molecules can be effectively exfoliated from MWCNT surfaces. This can be achieved as MWCNTs and dye molecules display different affinities to stationary and mobile phases in chromatography. When the mobile phase climbs up the TLC plate, a re-distribution of MWCNTs and dye molecules in these two phases is initiated and the outcome is the separation of these two species. We believe this general picture is applicable to other CNT/dye systems and this solubilization-separation process enables the applications of carbon nanotubes in textiles, dyeing, printing, and related industries.

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Figure captions

Figure 1. Photographs of vials of dye solutions (0.1 kg/m^3) and MWCNT(0.1 kg/m^3) /dye (0.1 kg/m^3) adduct dispersions. a) Direct Blue 106 (DB); b) MWCNT/DB; c) Direct Orange 39 (DO); d) MWCNT/DO; e) Direct Yellow 44 (DY); f) MWCNT/DY; g) Acid Red 91, (AR); h) MWCNT/AR.

Figure 2. AFM images of a) DY-functionalized MWCNTs; b) 3-D images.

c)

Figure 3. Chromatogram of MWCNT/DY adducts before (a) and after (b) separation. Spectra of dye, MWCNTs, MWCNT/dye adducts, and defunctionalized counterparts: c) FT-IR spectra; d) Raman spectra, 514 nm laser excitation.