

Raman and FT-IR studies on dye-assisted dispersion and flocculation of single walled carbon nanotubes

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Abstract Aqueous suspensions of single walled carbon nanotubes (SWCNTs) were prepared with the aid of dye molecules to form thermodynamically stable colloidal systems. By adding sodium chloride electrolyte, SWCNTs flocculated and settled out due to the destabilization of colloidal systems initiated by the increase in ionic strength. The dye molecules were removed by heat treatment at 300°C for 5h following washing with water. Raman spectroscopy was used to monitor the whole procedure. The resulting spectra confirm the non-destructive dispersion and flocculation of SWCNTs and the complete removal of the dye molecules; Fourier transform infrared spectroscopy also confirmed this.

Keywords: Single walled carbon nanotube, Raman spectroscopy, Fourier transform infrared spectroscopy, colloid, dye

1. Introduction

Single walled carbon nanotubes (SWCNTs) distinguish themselves as a new class of materials due to their unique electrical and mechanical properties and are widely used

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as electronics, sensors, composites fibres, and field emission materials [1,2]. Owing to their large mass, SWCNTs precludes them from being soluble in aqueous media, which significantly reduces their processability and limits their applications [3]. Polymers and biomolecules can suspend SWCNTs in aqueous media, but the removal of attached large moieties after processing is problematic [4-6]. Noncovalent modification of SWCNTs with surfactants is also recognized as an efficient method to disperse SWCNTs in water and the suspended individual SWCNTs can be driven out of water by either high force centrifugation or microfiltration [7-9]. Both are costly, time consuming and not amenable to scale up. Research is still necessary to establish how SWCNTs can be effectively dispersed into and separated from the aqueous phase afterwards, which is of great importance for the purification and functionalization of nanotubes. In this study, we use organic dyes to disperse SWCNTs into water and, with the aid of electrolyte, SWCNTs are flocculated and precipitated. By washing and heat treatment the dye molecules are removed completely. Moreover, less expensive optical spectroscopies (Raman and Fourier transform infrared, FT-IR) are adopted to monitor the whole procedure and evidence the removal of dye molecules. This is a fast, economic and non-destructive technique, allowing large amounts of SWCNTs to be manipulated in aqueous phase and simplifying their use as chemical reagents.

2. Experimental

2.1. Materials.

Direct Orange 39 (Colour Index: 40215) was supplied by Kemtex Education Supplies (UK). SWCNTs (purity: 70%) and SWCNTs (purity: 50%) were obtained from Nanocyl S. A. (Belgium) and NanoLab (US), respectively. All these commercial products were used as supplied.

2.2. Dispersion and flocculation of SWCNTs.

A typical procedure is given below: dyes (20 mg) and SWCNTs (10 mg in 100 cm³ deionized water) were sonicated in QS 10 ultrasonic bath (Ultrawave Ltd. UK) for 20 mins. After centrifugation in Espresso (Thermo Electron Corporation, France) at 4,000 g for 40 mins, the supernatant was carefully decanted and whilst stirring, sodium chloride (30 g) was gradually added. The resulting mixture was then filtered on 0.1 μm polycarbonate membrane and rinsed with water until the filtrate turned from orange to colourless. The retained SWCNTs were then annealed at 300 °C for 5 hrs.

2.3 Characterization.

SWCNT suspensions (20 μl) were spin coated on silicon wafer and dried for the Raman spectra record (Renishaw System 2000 microRaman spectrometer, Renishaw, UK). SWCNTs and dyes were ground with potassium bromide (KBr) salt to make pellets for FT-IR analysis (a Nicolet 460 FT-IR spectrometer, US).

3. Results and discussion

3.1. Dispersion and flocculation of SWCNTs

Figure 1 displays the different physical states of SWCNTs in deionised water. When SWCNTs are introduced, the dye solution becomes much darker (Fig. 1b and 1d) with respect to the pure dye solution (Fig. 1a), indicating the generation of SWCNT colloids in water. After the addition of sodium chloride (NaCl), SWCNTs become flocculated and settle at the bottom of the vials (Fig. 1c and 1e), suggesting the destabilization of SWCNT colloids.

The dispersion and flocculation of SWCNTs may be explained using the theory of Derjaguin, Verwey, Landau and Overbeek [10,11], which suggests that the stability of a particle in solution is the balance of competing contributions between attractive van der Waals forces and electrical double layer repulsive forces that exist between particles as they approach one another. When the repulsive forces prevail, a thermodynamically stable colloid system can be expected. However, if the attractive forces predominate, the particles will become destabilized and result in flocculation.

The skeleton of dye molecules is made up of benzene rings and nitrogen-nitrogen double bonds (-N=N-), allowing the delocalization of electronic charge and the formation of extended π -conjugate system (see Figure 3 for the chemical structure of dye molecule); whereas nanotubes have delocalized π -electrons along the nanotube axis [12]. When mixed with SWCNTs in water, dye molecules orient themselves in such a fashion that benzene rings face toward nanotube surfaces and initiate the π - π stacking [13]. As a result, dye molecules are adsorbed on nanotubes and impart negative charges to SWCNT surfaces, since the sodium sulfonate groups (-SO₃Na) become dissociated and yield anions (-SO₃⁻) in water. By electrostatic forces, cations (Na⁺) are attracted and closely attached to the SWCNT surfaces; this liquid layer is similar to the Stern layer. Beyond this layer, there exists a less firmly associated outer layer containing free ions with a higher concentration of Na⁺, which can be called the diffuse layer. The electric double layer structure of SWCNT colloids can be represented diagrammatically as dispersed SWCNTs in Figure 2.

Owing to the stronger repulsive forces provided by this electric double layer, individual SWCNTs can be dispersed in water with the formation of colloids. When

NaCl is introduced, the ionic strength in solution is boosted and this will bring about compression in the electrical double layer; the higher the ionic strength, the more compressed the double layer becomes. A direct consequence of this decrease in thickness is the drop of the repulsive forces. When the ionic strength is sufficiently high, the van der Waals can overcome the electric repulsive forces and become the dominant factors in controlling the interactions between SWCNT colloids. Thus, if SWCNT colloids collide with one another due to Brownian motion, convection, or gravity, they can aggregate and flocculate. This dispersion and flocculation procedure is depicted in Figure 2. It is worth pointing out that the application of a gentle stirring is beneficial for promoting settling rate as the stirring can bring small flocculations into contact with each other and produces large ones. Apparently, the increase in flocculation dimension will facilitate its settling due to the effect of gravity forces.

3.2. Removal of dye molecules

When organic molecules are employed to disperse carbon nanotubes, care must be taken as the residual molecules attached on nanotubes can dramatically deteriorate the tube's properties, presumably owing to the insulating nature of organic molecules [14]. Raman and FT-IR spectroscopies are convenient and powerful techniques in characterizing the chemical structure of dye molecules as dye molecules generally possess functional groups that exhibit strong signals in the spectra and can be easily identified. Thus, these two techniques are applied here to evidence the removal of dye molecules. The Raman and FT-IR spectra of dye molecules are plotted in Figure 3 and Table 1 relates the characteristic frequencies to the vibrations of corresponding groups [15]. A comparison between the Raman and infrared spectra shows most of the frequencies within the 1000-1600 cm^{-1} region are common to both spectra and

coincide with each other, while those lower than 1000 cm^{-1} appear only in the infrared spectrum.

The Raman spectra of the flocculated SWCNTs, water rinsed SWCNTs and heat treated SWCNTs (SWCNT purity: 50%) are shown in Figure 4, normalized to G band intensity. As can be observed, pristine SWCNTs show the typical D-mode (1350cm^{-1}), G-mode (1590 cm^{-1}) vibration band and overtone of the D-mode (G' , 2680 cm^{-1}). SWCNTs also exhibit a radial breathing mode (RBM) band in low frequency range ($\sim 184\text{ cm}^{-1}$), indicating the individual SWCNTs have a diameters of $\sim 1.35\text{ nm}$ [16]. These characteristic bands also emerge in the spectra of the flocculated, washed, and heat treated solid samples, suggesting the existence of SWCNTs. It is also noticeable that the D-band intensity of all these treated SWCNTs is comparable with that of the pristine SWCNTs, implying that further nanotube destruction and creation of amorphous carbon impurities were avoided in the whole procedure.

The stretch of $\text{N}=\text{N}$ of dye molecules accounts for the appearance of strong Raman band at 1440 cm^{-1} , therefore this band was monitored to indicate the presence/absence of dye molecules. As shown in Figure 4, for the flocculated SWCNTs a strong $\text{N}=\text{N}$ stretching band can be identified, suggesting the abundance of dye molecules. After rinsing with deionised water, this band is greatly depressed but still identifiable. This means most of dye molecules are washed away but not completely, which reflects the amphoteric properties (hydrophilicity and hydrophobicity) of dye molecules. The presence of the strongly polar ($-\text{SO}_3^-\text{Na}^+$) group prefers to interact with water, and thus dye molecules can be carried away by water. In the meantime, dye molecules can be adsorbed on nanotubes through π - π stacking, leading to the difficulty of complete

desorption. After heat treatment, the N=N stretching band disappears, implying the deficiency of dye molecules. This is largely because the residual organic dye molecules are decomposed in this process.

The resulting SWCNTs were also analysed with FT-IR and the infrared spectra were shown in Figure 5. For the flocculated SWCNTs the benzene C=C stretch frequency ($\sim 1590\text{ cm}^{-1}$) and benzene C-H deformation frequency ($\sim 1180\text{ cm}^{-1}$) can be observed, indicating the presence of dye molecules. The profiles of the infrared of the heat treated SWCNTs do not exhibit these frequencies, suggesting that dye molecules are absent. While for the water rinsed SWCNTs, the absorption frequencies arising from the residual dye molecules can not be observed. This is presumably because the black SWCNTs can absorb infrared radiation and conceal the infrared signals stemming from the trace amounts of dye molecules.

4. Conclusions

SWCNTs were dispersed in dye solutions *via* the formation of colloidal systems due to the amphoteric properties, *i.e.* hydrophilicity and hydrophobicity, of the dye molecules. The introduction of NaCl promotes the suspended SWCNTs to form flocculation and settle out. This may result from the increase in ionic strength, which considerably compresses the electric double layer and reduces its thickness, leading to the drop of the repulsive forces between SWCNT colloids and subsequently the destabilization of the colloidal systems. Most dye molecules can be washed away, which is in accordance with their hydrophilic properties. The residual dye molecules can be completely removed by heat treatment due to the decomposition of organic molecules. Raman and FT-IR spectroscopies evidence the removal of dye molecules

and it is likely that this technique is applicable to other carbon nanotube and dye systems.

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Figure captions

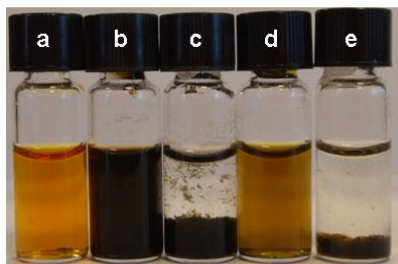


Figure 1 Photographs of vials of dye solution: a) 0.2 kg/m^3 , SWCNT (0.1 kg/m^3)/dye (0.2 kg/m^3) dispersions: b) 70% SWCNTs, d) 50% SWCNTs, and flocculated SWCNTs: c) 70% SWCNTs, e) 50% SWCNTs.

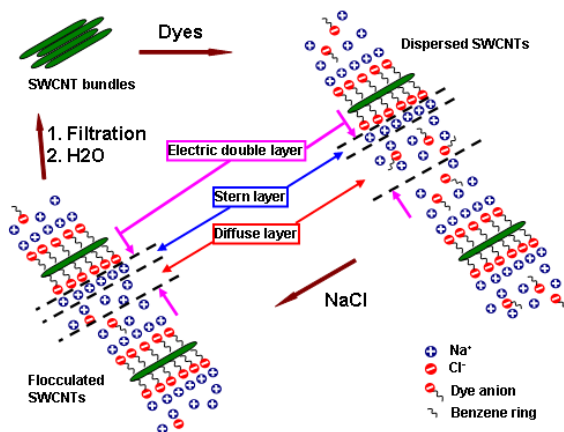


Figure 2 Schematic of the dispersion and flocculation of SWCNTs.

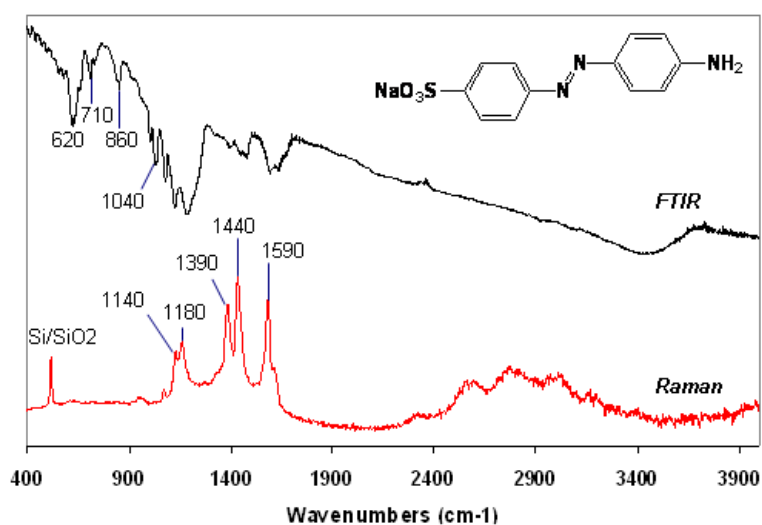


Figure 3 FT-IR transmittance and Raman absorbance spectra of dyes.

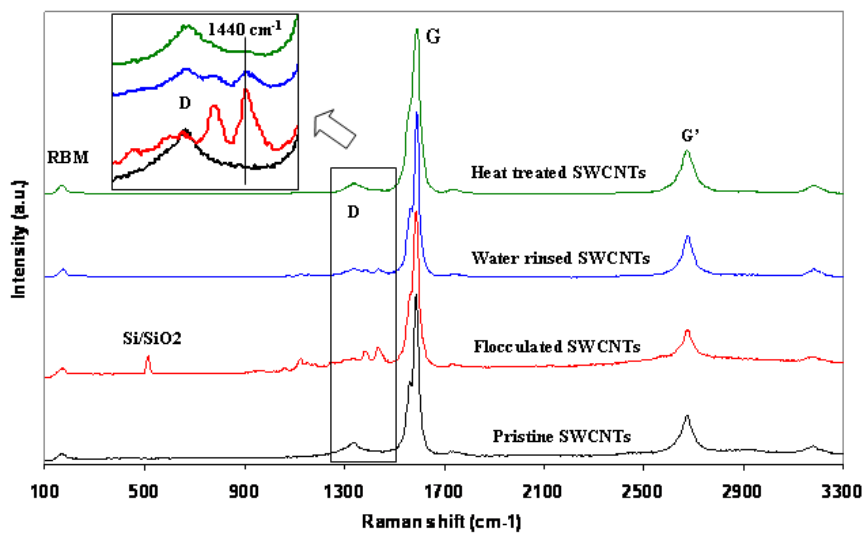


Figure 4 Raman spectra of the SWCNTs. Excitation at 514 nm.

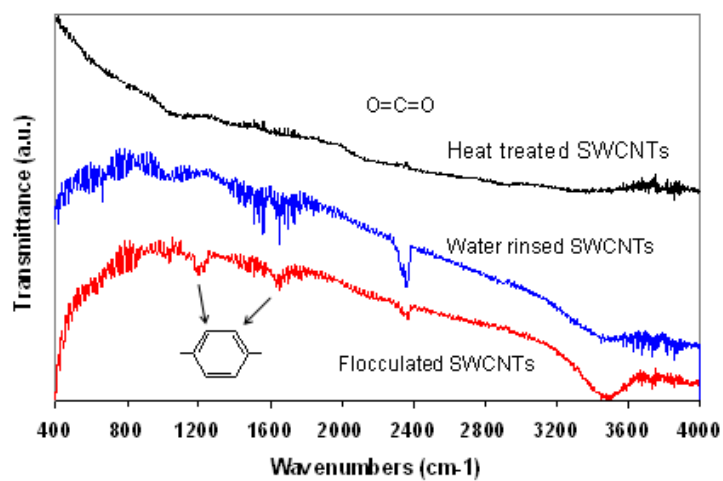


Figure 5 FT-IR spectra of the SWCNTs.

Table captions

Table 1 Assignment of FT-IR and Raman frequencies

Vibrations	Infrared (cm^{-1})	Raman (cm^{-1})
C=C stretch	1590	1590
N=N stretch	1440	1440
C-H deformation	1390, 1180,1040	1390,1180,1040
C-N stretch	1140	1140
C-S asymmetric stretch	860	Absent
C-H out-of-plane bend	710	Absent
C-S symmetric stretch	620	Absent