

Effect of Alkyl Chain in Quaternary Ammonium Dispersants on the Suspension of Multi-Walled Carbon Nanotubes

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Abstract

Cetyltrimethylammonium Bromide (CTAB) and Dodecyl Trimethyl Ammonium Bromide (DTAB) were used to non-covalently functionalize Multi-Walled Carbon Nanotubes' (MWCNTs') surfaces. Transmission electron microscopy analyses evidenced the debundling effects of these two cationic dispersants on MWCNT aggregates. The intensity of G band relative to D band in Raman profiles of MWCNTs does not change substantially after the suspension, indicating the majority of the sp^2 structure of MWCNTs is preserved well. There exists a critical concentration for both CTAB and DTAB in suspending MWCNTs, i.e. 0.1 g/l, which can be ascribed to the formation of dispersant micelles. CTAB is superior to DTAB in suspending MWCNTs at a concentration lower than the critical one, but a reverse trend is observed when the concentration is beyond the critical one; this is interpreted in terms of geometric features of alkyl chains.

Keywords: Alkyl chain, Carbon nanotube; Suspension; Surface modification; Quaternary ammonium dispersant

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Introduction

Carbon Nanotubes (CNTs) have been proposed as promising materials for a number of applications on the basis of their unique electronic and structural properties. Quite often, if not always, as-produced CNTs contain large amounts of bundles and ropes, originating from the strong van der Waals forces, approximately 500 eV per micrometer tube-tube contact [1]. For many applications, it is necessary to separate these bundles/ropes into individual nanotubes. Owing to the presence of lone pair of electrons, organic amines and amides have been attempted to suspend CNTs [2, 3]. The effect of alkyl chain on the interaction of amides with CNTs has also been explored elaborately. The introduction of alkyl chain to amide can thermodynamically stabilize the double bond character in the resonance-stabilized amide, resulting in the stabilization of the electronic dipole moment and in turn, enhancing the induced dipole-dipole interaction between amide and CNTs [4, 5]. In parallel, organic ammoniums have been applied to suspend CNTs, but the influence of alkyl chain in organic ammonium on the interactions with CNTs is not specific clear [6]. In this study, Cetyltrimethylammonium Bromide (CTAB) and Dodecyl Trimethyl Ammonium Bromide (DTAB) were used to suspend Multi-Walled Carbon Nanotubes (MWCNTs). CTAB and DTAB molecules carry the same amount of electric charge, but the former has a longer alkyl chain being attached to ammonium nitrogen. As such, the comparison of the suspending power of CTAB and DTAB will demonstrate the effect of alkyl chain, and enrich our

understanding on the interaction between organic quaternary ammoniums and CNTs.

Experimental

Materials

Multi-Walled Carbon Nanotubes (MWCNTs) with outer diameter and length falling in the range of 10-20 nm and 5-15 μm , respectively, was obtained from Shenzhen Nanotech Port Co. Ltd. (China). Cetyltrimethylammonium Bromide (CTAB, purity: 99%) and dodecyl trimethyl ammonium bromide (DTAB, purity: 98%) were kindly supplied by Tianjin Guangfu Fine Chemical Research Institute (China). All chemicals were used as received.

Suspension of MWCNTs

A certain amount of CTAB was added to 8 ml de-ionized water and then 5.0 mg MWCNTs was mixed with the above solution under mechanical stirring. The resultant mixture was ultrasonicated for 60 min with a power of 750 W and centrifuged at 10,000 rpm for 15 min in sequence. The supernatant was then decanted with care for further analyses. Similarly, MWCNTs were suspended in de-ionized water with the aid of DTAB.

Characterization of MWCNT Suspension

The thermogravimetry analysis were carried out on a Thermo Gravimetric Analyzer (TGA/SDTA851, Mettler-Toledo, US) in air with a temperature increasing rate of $10^\circ\text{C}/\text{min}$. Ultraviolet-visible-near infrared (UV-Vis-NIR) spectra were recorded on a UV-Vis-NIR scanning spectrophotometer (Cary 5000, Varian Ltd., UK). Quartz cuvette with 10 mm optical path length (CXA-145-055M, Fisher Scientific, UK) was adopted as the solution holder. The suspension was dropped and cast on a silica wafer. The Raman spectra of deposited samples were then recorded on a Renishaw Invia microRaman spectrometer (UK) with an excitation wavelength of 632.8 nm. Transmission Electron Microscopy (TEM) images were obtained on a TG 220 S-Twin JEM-100CX II (FEI, US).

Results and Discussion

TGA of MWCNTs

TGA is widely used to quantitatively characterize carbon nanotubes, and this is on the assumption that under oxygen, carbon nanotubes will pyrolyze leaving any inorganic residue behind, quite possibly in the form of its corresponding oxides. TGA profile of as received MWCNTs is depicted in (Figure 1), wherein there is a major mass-loss event that occurs, indicated by the drop of the weight percent of MWCNTs from 99.1% to the residual value of 2.4%, which is related with the burning of MWCNTs. Derivative of Thermogravimetry (DTA) curve demonstrates that the burning of MWCNTs reaches its maximum rate at around 649°C . The trace weight loss below 500°C is believed to be associated with the evaporation of water and the burning of amorphous carbon.

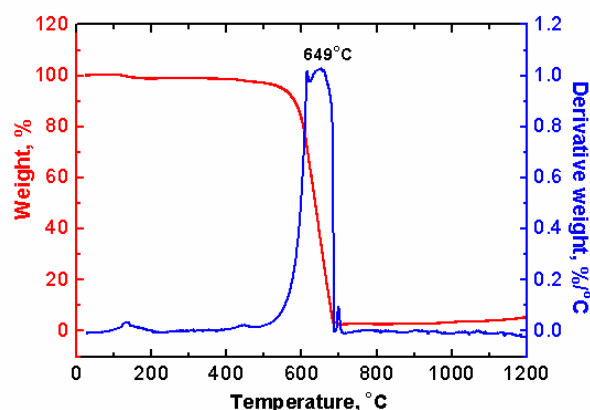


Figure 1: TGA and derivative TGA profiles of MWCNTs

Suspension of MWCNTs

(Figure 2) are the photographs of MWCNT suspensions in water with and without dispersing agents. In contrast to pure water, the dispersant solutions display much deeper colour after the suspension of MWCNTs, implying the dispersants have a positive role to play in terms of suspending MWCNTs. Another concern with regard to the suspension of carbon nanotubes is the stability of suspensions, i.e. how long it will take for the separated individual carbon nanotubes to reaggregate and precipitate. After four weeks, the MWCNTs remain well suspended in water and no MWCNT sediments were observed,

demonstrating that the prepared MWCNT suspensions have good shelf lives.

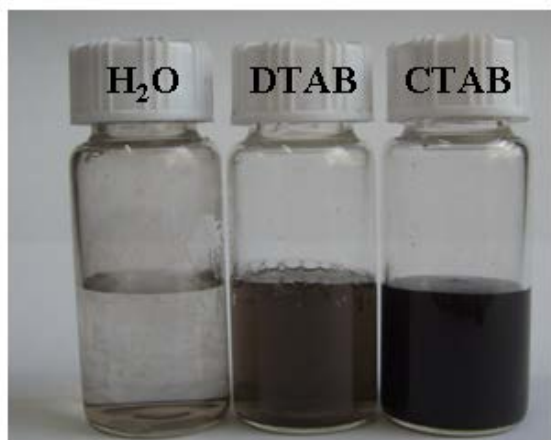


Figure 2: Vials of MWCNT suspensions after four weeks, DTAB (0.1 mg/ml), CTAB (0.1 mg/ml)

TEM images (Figure 3) display the effect of dispersants on the separation of MWCNT bundles. Without dispersants, MWCNTs were bundled and entangled together (Figure 3a). When dispersants were involved in solution, the bundle size is reduced substantially and individual carbon nanotubes are clearly visible (Figure 3b). High resolution TEM reveals the outer diameter of individual nanotubes is about 20 nm (Figure 3c).

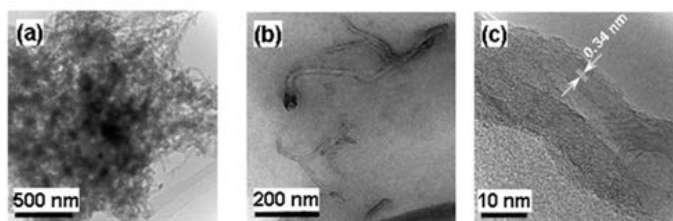


Figure 3: TEM images of raw MWCNTs (a) and CTAB suspended MWCNTs (b, c)

Raman Studies

Raman spectroscopy has proved to be a popular non-destructive technique successfully used in the micro-structural characterisation of carbon based materials. In the Raman spectra of MWCNTs (Figure 4), three bands are distinguishable. The G band, located at 1590 cm^{-1} , corresponds to the tangential stretching mode of highly oriented pyrolytic graphite, which is indicative of the presence of crystalline graphitic carbon in the

CNTs. The D band, located at 1330 cm^{-1} , originates from the disorder induced features due to defect and finite particle size effect. The second-order band of D at 2670 cm^{-1} (G') is also identifiable in the spectra.

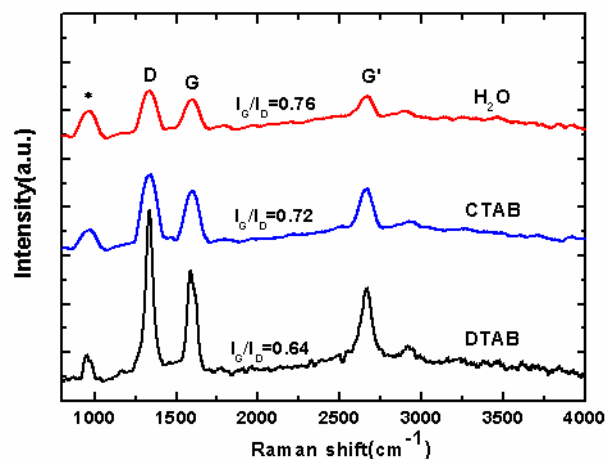


Figure 4: Raman spectra of raw MWCNTs and suspended MWCNTs

The intensity of G band relative to the intensity of D band (I_G/I_D) is often used as a measure of the structural purity of graphitic materials and the amount of disorder in carbon nanotubes. The I_G/I_D ratios of DTAB and CTAB suspended MWCNTs are 0.72 and 0.64, respectively. Compared with that of raw MWCNTs being 0.76, these ratios decrease, albeit quite small. This suggests a bit more defect content in the dispersant-suspended MWCNTs, which may be attributed to the effect of ultrasonication. The high and localized ultrasonic energy may induce new defects on the sidewalls and/or ends of nanotubes [7].

Effect of Dispersant on the Suspension of MWCNTs Critical Dispersant Concentration

To characterize carbon nanotubes in solution quantitatively, optical absorption spectroscopy has been widely used; this can be achieved because the absorption intensity is proportional to the quantity of nanotubes suspended in a solution [8]. The UV-Vis-NIR spectra of CTAB and DTAB suspended MWCNTs were recorded and are shown in (Figure 5). The absorbance of

MWCNTs suspended with different contents of dispersants at 800 nm is plotted in insets to (Figure 5).

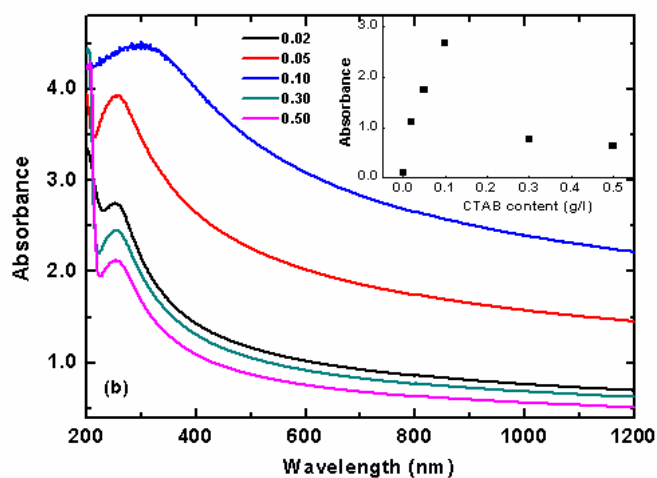


Figure 5: UV-Vis-NIR absorbance spectra of MWCNT suspensions with different dispersant contents: (a) DTAB, (b) CTAB. Inset: absorbance of MWCNT suspensions at 800 nm

(Figure 5) and its insets demonstrate that there is a critical content for both CTAB and DTAB in suspending MWCNTs, *i.e.* 0.1 g/l. Below this critical content, the absorbance of MWCNT suspensions increases with the increase of dispersant content. Beyond this critical content, the absorbance decreases with the increasing dispersant content. This can be ascribed the formation of dispersant micelles. When the dispersant content is lower than the critical value, more MWCNTs are suspended in water with the increase of dispersant content, resulting in the increase of absorbance. Concurrently, with the increase of dispersant content, the possibility for dispersant molecules themselves to aggregate together and form micelles is raised. When reaching a given content (0.1 g/l) dispersant molecules start to form micelles. If the size of the generated micelle is sufficiently large and can not penetrate into the space between the separated MWCNTs, these micelles will impose an inward force, analogous to the osmotic pressure and proportional to the dimension of micelle, onto the suspended individual MWCNTs. This is in line with the model developed by Asakura and Oosawa, where the interactions between two parallel plates immersed in a solution of macromolecules were investigated extensively [9]. As a result, the separated MWCNTs re-

aggregate and become optically inactive, lowering the population of individual MWCNTs in water. These results enable one to conclude that the content of dispersant is the decisive parameter that governs the suspension of carbon nanotubes, instead of the mass ratio of MWCNTs to dispersant.

Suspending Power of Dispersants

To compare the suspending power of CTAB and DTAB, the MWCNT amounts suspended in water were calculated in accordance with Beer-Lambert's law (Eq. (1)).

$$A = \log \frac{I_0}{I} = \varepsilon \cdot C \cdot l \quad (1)$$

Where in A is the absorbance, ε is the molar extinction coefficient of MWCNTs and was evaluated to be $35.10 \text{ ml} \cdot \text{mg}^{-1} \text{ cm}^{-1}$ at 800 nm [10], l is the light path length and equals the length of quartz cuvette (1 cm). The MWCNT contents as a function of dispersant content are plotted in (Figure 6). It is worth pointing out that both CTAB and DTAB do not exhibit observable absorbance at 800 nm and thus the presence of dispersants does not affect the calculation of MWCNT concentrations in water.

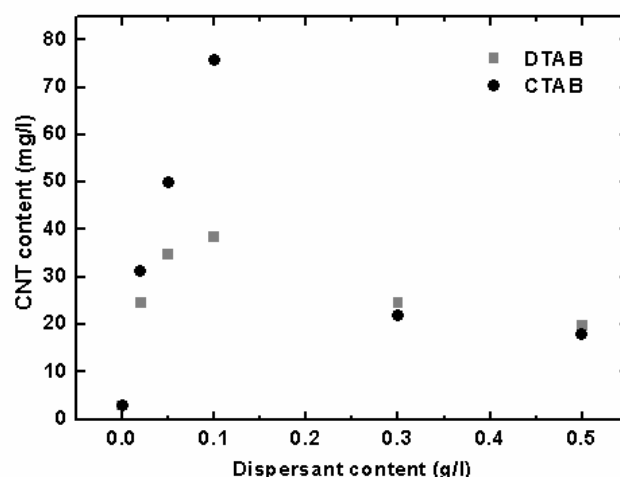


Figure 6: Variation of suspended MWCNT content in water against dispersant content

Apparently, when the dispersant content is lower than the critical value, 0.1 g/l, at the same dispersant content, the amount of MWCNTs suspended in CATB solution is much larger than that in DTAB. That is to say, CTAB demonstrates better

suspending power than DTAB. In 0.1 g/l CTAB solution, 75.7 mg/l MWCNTs can be suspended; whereas only 38.5 mg/l MWCNTs can be suspended in 0.1 g/l DTAB solution. This is in agreement with the result demonstrated in Section 3.2, *i.e.* CTAB-MWCNT suspension turns out to be much darker than DTAB-suspended one. When the dispersant content is over 0.1 g/l, the amount of MWCNTs suspended in DTAB solution is slightly higher than in CTAB.

In water, both CTAB and DTAB undergo dissociation, yielding a quaternary ammonium with an alkyl chain and a bromide ion. When mixed with MWCNTs, the resulting ammonium will arrange itself in such a manner that the hydrophobic alkyl chains interact with MWCNTs and become adsorbed onto MWCNTs, and the hydrophilic ammonium orients towards water. Relying on the electrostatic repulsive forces generated between ammonium ions and the steric hindrance offered by the alkyl chains, the attractive van der Waals forces between MWCNTs can be overcome effectively and individual MWCNTs can be obtained. There is no doubt that an ideal dispersant molecule is one that can adsorb on nanotubes efficiently and provide high steric hindrance and electrostatic repulsion. To investigate the effect of stereo structure of alkyl chains on the suspension of MWCNTs, we have conducted AM1 theoretical calculation using Chem 3D MOPC to determine the geometric features of CTAB and DTAB. The 3-D structure of CTAB and DTAB are shown in (Figure 7).

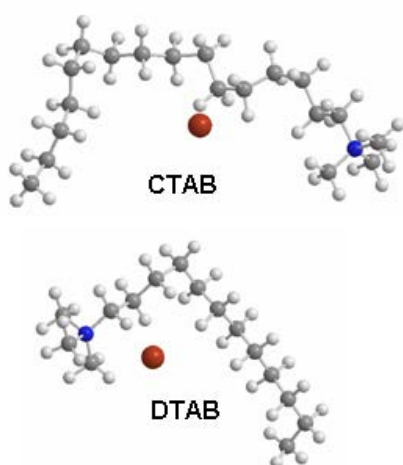


Figure 7: Stereo structures of CTAB and DTAB, red: bromine, blue: nitrogen, dark grey: carbon, light grey: hydrogen

Considering the length of alkyl chains involved here (over 12-carbon), when adsorbing onto a nanotube surface, it is probably energetically favorable for the alkyl chains to bend around the circumference of the nanotube. (Figure 7) exhibits that CTAB has a longer and zigzagged structure; in contrast, DTAB possesses a shorter and relatively straighter structure. As a consequence, the efficiency of the interactions between CTAB and MWCNTs can be expected to be higher, presumably owing to the enhanced C-H $\cdots\pi$ interactions. This is in good agreement with the results obtained in Section 3.4. Below critical content, CTAB exhibits higher dispersing power than DTAB, and this can be ascribed to the stronger interaction of CTAB with MWCNTs. In MWCNT suspensions, the dissolved dispersant molecules can exist as free molecules in water or adsorb onto MWCNTs. CTAB molecules have a much stronger propensity to interact with MWCNTs, whereas DTAB molecules are relatively inclined to exist as free molecules. As such, at an identical dispersant content, the proportion of CTAB that interacts with MWCNTs is higher than that of DTAB, and thereby more MWCNTs can be suspended. It is also noteworthy that, once adsorbing on MWCNTs, aside from the electronic repulsion, CTAB molecules may create a higher steric hindrance between MWCNTs due to its longer alkyl chain. This will contribute to the stabilization of suspended MWCNTs and promote the suspending power of CTAB. On the other hand, once forming micelles, the dimension of CTAB ones is expected to be larger than that of DTAB due to the presence of a longer and zigzagged alkyl chain. This will result in higher inward forces on suspended MWCNTs, since the inward force is proportional to the dimension of micelle [9]. Obviously, this will give rise to the re-aggregation of MWCNTs and reduce the amount of individual MWCNTs in solution. And this explains why DTAB exhibits higher dispersing power than CTAB when the dispersant content is over critical value.

Conclusion

MWCNTs can be effectively suspended in water with the aid of CTAB and DTAB, and CTAB exhibits stronger suspending power than DTAB when the dispersant content is lower than the

critical concentration (0.1 g/l). This is because CTAB has a much zigzagged and longer alkyl chain, which facilitates its interaction with MWCNTs through the promoted C-H $\cdots\pi$ interaction and improves the stabilization of suspended MWCNTs by providing a higher steric hindrance. When the dispersant content is over 0.1 g/l, CTAB is inferior to DTAB with regard to suspending MWCNTs. This may be explained in terms of the effect of dimension of dispersant micelles, resulting in the re-aggregation of suspended MWCNTs.

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