Discrete dispersion of single-walled carbon nanotubes†

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Single-walled carbon nanotubes (SWNTs) have been effectively wetted and dispersed in saturated sodium hydroxide (NaOH) alcohol–water solutions with little surface damage or shortening of the tubes; the treated material was dissolvable as individual tubes in many common organic solvents.

There is a wide range of potential applications for SWNTs which harness their unique electronic, thermal, optical and mechanical properties. A significant difficulty in realising these applications is that, while the majority require individually dispersed nanotubes, SWNTs tend to form as rope-like bundles due to their long aspect ratios (>1000) and the strong anisotropic interactions between them (0.5 eV nm^{-1}).[1] Additionally, the bundles can be highly contiguous, making them difficult to disperse in both organic and aqueous media.

Numerous attempts have been made to develop an effective method to discretely disperse SWNTs at high concentrations.[2–4] These approaches have included the chemical functionalization of the tubes' sidewalls with carboxylates and amines[6] and scission of tubes by mechanical milling.[5] Surfactants,[7,8] small organic molecules[9,10] and macromolecules[11,12] have also been used to coat the surfaces of the tubes. However, these methods are not ideal since the physical shortening and chemical processing of SWNTs often damages their structure. Here, we report that SWNT bundles can be discretely dispersed in a saturated NaOH alcohol–water solution with almost full dispersion occurring when the treated tubes are transferred to other solvents. Additionally, the SWNTs treated in this way appear to retain their pristine tube structure while showing improved purity.

The SWNTs used in this work were produced by the catalytic vapour decomposition of methane over an iron catalyst supported on magnesium oxide, the support being subsequently removed using an acid wash.[13] The NaOH–ethanol solutions contained 150 g l^{-1} of NaOH in 80 vol% ethanol and 20 vol% water. Normally, as-prepared SWNTs tend to agglomerate into hard and dense aggregates after acidic purification. However when the nanotubes were immersed into the NaOH alcohol solution (10 mg SWNTs in 25 ml of solution), small air bubbles evolved from their surfaces and the aggregates swelled and softened such that they began to break up after a few minutes of gentle sonication. After ~5 h of this treatment in the ultrasonic bath a black slurry was formed which showed no signs of phase separation after several days. The slurry was filtered and washed thoroughly with a water–ethanol (volume ratio 1 : 5) mixture until the pH of the filtered solution was neutral and then washed twice with absolute ethanol to remove any water. Finally, it was either dried under vacuum at room temperature or kept dispersed in alcohol.

Fig. 1 shows the typical TEM images of SWNTs before and after the treatment in NaOH alcohol solution. Before treatment, as-prepared SWNTs could not be dispersed easily in ethanol even with ultrasonication, and were mainly in entangled bundles between 20 and 50 nm in diameter. Treatment in the NaOH ethanol system dispersed the entangled SWNTs to form finer bundles with the average bundle diameter dropping to less than 8 nm, including a significant number of individual tubes. However, little change was observed on the length of tubes. The decrease in bundle size was further confirmed by the BET surface area of the sample increasing from 461 m^2 g^{-1} to 627 m^2 g^{-1} with the treatment.

It is interesting to note that the filtered solution from the washing of the SWNT slurry was light yellow, suggesting that some of the catalytic iron particles have been removed from the SWNTs. This hypothesis was confirmed by thermal gravimetric analysis (TGA) (shown in supporting materials†); the residue after heating to 850 °C in air was mainly iron oxide and represented 2.5 wt% and 8.3% for the treated and as-prepared samples respectively. TGA also indicated that while both of the samples started to burn at ~400 °C, the weight loss peak was significantly sharper for the treated material (400–700 °C) than the untreated SWNTs (400–850 °C). The difference is believed to be due to the higher surface area of the treated, debundled material giving more uniform contact with the air and enabling more efficient combustion.

It was found that after the treatment, the SWNTs became even more hydrophobic and difficult to disperse in water. However, the tubes could be easily re-dispersed in most common organic solvents, such as *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, tetrachloroethylene,

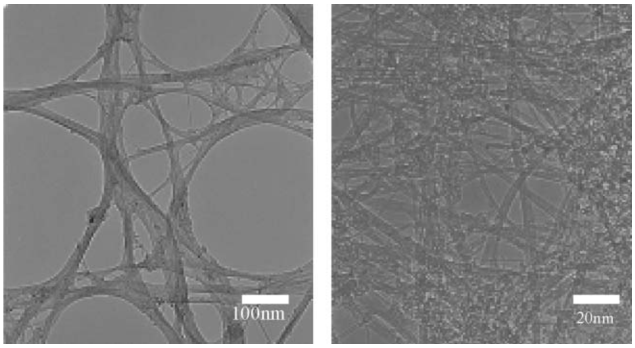

Fig. 1 TEM images of as-prepared SWNTs (left) and treated SWNTs (right) obtained by dispersing them in ethanol.

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† Electronic supplementary information (ESI) available: TGA data and Raman spectroscopy are available. See http://www.rsc.org/suppdata/cc/b4/b419039d/
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N-methyl-2-pyrrolidinone (NMP) and epoxy resin. Unlike as-prepared SWNTs, the treated SWNTs could be dissolved in NMP in concentrations up to 8 mg ml^{-1} and with little sediment after sitting for several weeks (Fig. 2A). (This solubility compares favourably to other methods which typically achieve $\sim$1 mg ml^{-1}.) Atomic force microscopy (AFM) of the treated nanotubes re-dispersed in THF found that the average size of the fibrous entities was in the range 1.2–3 nm (Fig. 2B), revealing that the treated SWNTs could be further dispersed as individuals in the organic solvent.

Generally, a medium for the isolation and dissolution of SWNTs has to be capable of both wetting the hydrophobic tubes' surfaces and then modifying these surfaces to decrease the interaction between tubes. For example, previously high-concentration surfactant solutions[7] and concentrated superacid solutions[14] have been found effective in making SWNT suspensions since the tubes' surfaces can be wetted and charged by the adsorption of surfactant molecules or protonation of SWNTs in superacids. However, both of the methods can damage the nanotubes' structure and the treated tubes are only dispersable in aqueous solutions.

In order to evaluate the effectiveness and understand the dispersion mechanism of the NaOH–ethanol treatment, comparative studies were made with concentrated NaOH aqueous solution (150 g l^{-1}) and 10% hydroxylamine hydrochloride acid solution. (The latter solvent was described recently by Sabba and Thomas[10] who found that this amine solution dispersed the SWNT bundles by charging the tube surface through the adsorption of NH_3OH^+ ions.) As Fig. 2A shows, the aqueous hydroxide and amine solutions did not achieve as stable a dispersion as the treatment presented here. One reason for this difference between the treatments is believed to be that the alcohol NaOH solution was significantly better at wetting and thus softening and dispersing the as-produced nanotube aggregates. This idea was further supported by using successfully other alcohol solutions such as propanol and butanol. It should also be noted that alcohol NaOH solutions are commonly used to remove grease and other organics from glassware.

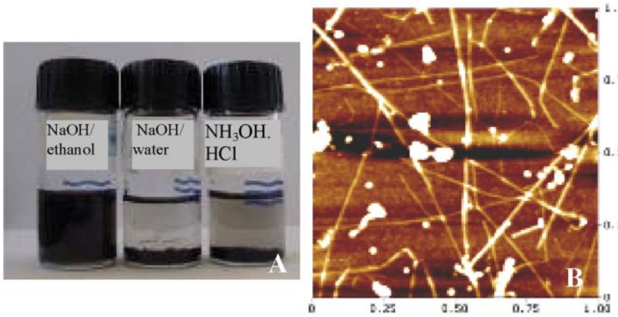

Fig. 2 (A) Vials containing 8 mg ml^{-1} SWNT dispersions in NMP after the treatment in (left to right) NaOH–ethanol solution (I), NaOH aqueous solution (II) and $NH_3OH{\cdot}HCl$ solution (III). Samples II and III were imaged after sitting for 1 day, while sample I was much more stable and imaged after three weeks. (B) Tapping mode AFM image of SWNTs treated in NaOH–ethanol solution spread on a Si surface from THF solution (0.1 mg ml^{-1}). The scale is in microns.

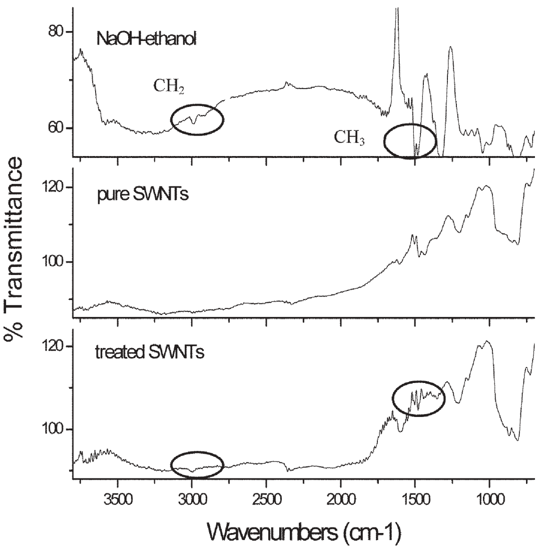

Fig. 3 FTIR spectra of pure SWNTs, treated SWNTs and the residue from the drying of NaOH–ethanol solution.

Spectroscopy was used in order to understand how the solution modified the surface of the nanotubes once it had wetted them. FTIR found no evidence for the hydroxylation of SWNTs (Fig. 3) but there were weak adsorption bands around 2923 cm^{-1} (asymmetrical and symmetrical stretching of CH_2 groups) and 1463 cm^{-1} (asymmetrical and symmetrical bending vibrations of CH_3 groups) that could be ascribed to the adsorption of sodium ethoxide (CH_3CH_2ONa) or ethanol on the tubes.[15] Energy dispersion X-ray analysis found further evidence for the adsorption of sodium ethoxide, with typically 4 wt% sodium remaining adsorbed onto the nanotubes after the sample had been thoroughly washed. Raman spectroscopy found a small increase on the ratio of $I_G : I_D$, confirming that the pristine tube structures of SWNTs were not damaged by this treatment (see supporting materials†). The emergence of some new radial breathing mode peaks in the Raman spectra revealed that due to the discrete dispersion of SWNT bundles, more detailed information on the diameter distribution of SWNTs could be observed. These new peaks remained whether the sample was in its wet form or dry form, implying that the vacuum drying of the treated material at room-temperature did not give rise to the obvious re-bundling of tubes.

The overall spectroscopic evidence indicates that the debundling of SWNTs in NaOH–ethanol solution was a physical rather than a chemical process since there was no evidence of covalent bonds. As a result, it is considered the NaOH solution rapidly wets the nanotubes and the small ions (sodium ethoxide and/or alcohol) easily diffuse into the bundles. These ions adsorb on the walls of the nanotubes, reducing the inter-tube forces such that the tubes are discretely dispersed.

In summary, treatment by NaOH in ethanol–water can effectively debundle SWNTs without any noticeably shortening or other damage. The treated SWNTs increased in purity and specific surface area and can be further debundled and dissolved in many common organic solvents. Overall, the treatment is simple, low-cost and potentially scalable.

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