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# Ultra-fast and scalable sidewall functionalisation of single-walled carbon nanotubes with carboxylic acid

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**A simple and fast method for the functionalisation of single-walled carbon nanotubes with carboxylic acid terminated molecules, at varying molar fractions, is presented.**

The electrical, thermal and mechanical properties of carbon nanotubes,[1] combined with their small size,[2] offer considerable potential for many applications, *e.g.*, integrated circuit interconnects and drug delivery.[3] However, as-produced CNT are challenging to process, as they tend to bundle into insoluble aggregates. To solve this problem, much research has been carried out on the functionalisation of CNT.[4] This approach has the added advantage that functionality can be used to tune CNT properties.[5–11]

One of the most useful functional groups is carboxylic acid, as it enables solubility of the nanotubes in water while, for example, providing a functional handle for amide bond formation. To the best of our knowledge, there is only one procedure for covalently adding carboxylic acid to the sidewalls of single-walled carbon nanotube (SWNT).[12] This reaction takes on average ten days and offers little control over the extent of sidewall functionalisation, with an upper limit of 1 in 24 SWNT carbons modified.

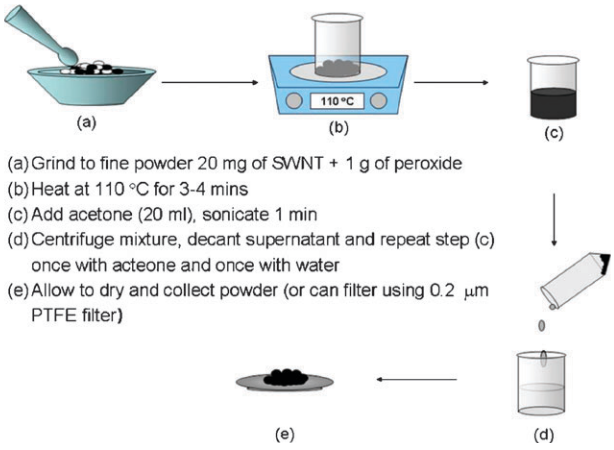
Herein, we report a modification of the published procedure[12] that enables a fast and intrinsically scalable functionalisation of SWNT (3–4 min) with a carboxylic acid moiety. It is shown that the degree of functionalisation can be incrementally controlled, the final amount of functionalisation is twice the best previously reported[12] and the carboxylic acid can be used for further facile reactions.

Scheme 1 outlines the procedure for the reaction. SWNT (20 mg) and succinic acyl peroxide (1 g) are ground to a fine powder. This powder is heated in a small beaker at 100 to 110 °C for 3–4 min.

Upon cooling the melt (a black liquid), acetone (20 ml) is added and the mixture is sonicated to disperse the SWNT and dissolve the excess molecule. After centrifuging, the supernatant is decanted, this last step is repeated once more with acetone and then water. After purification, the final solid can be left to dry and then collected. Otherwise it can be filtered over a PTFE filter (0.2 μm). The yield is in excess of 90%. To increase the number of functional groups on the SWNT sidewalls, the reaction procedure can be repeated. It was found that there was no increase in the number of functional groups after the fifth repeat reaction suggesting that the sidewalls were saturated.

This reaction procedure is a departure from the published one because it does not involve any solvent. The original reaction is performed in 1,2-dichlorobenzene at 90 °C for ten days. Carbon nanotubes can only be suspended in DCB through extensive sonication, and the peroxide molecule is not very soluble in DCB. Hence, the reaction happens in dilute conditions resulting in slow kinetics and poor yield. The strength of the new method is based around the low melting point of the peroxide molecule (100–110 °C), enabling us to use it as a solvent. The result is a reaction with much faster kinetics and improved yield. The higher temperature of the reaction (from 90 to 110 °C) affects the lifetime of the radical generated form peroxide that is known to be the reactive species in the reaction. It was reported that at 90 °C the half life of this radical is 60 min.[11] At higher temperatures it is reasonable to expect that it will be significantly shorter. We believe that this is the reason why we observe that, after 4 min, the reaction reaches completion as proven by the absence of further changes in the Raman spectrum of the product. The short lifetime of the radical also limits the extent of the reaction, but this is not a limitation of our approach as the reaction can be repeated multiple times.

Fig. 1 shows a photograph of four vials containing saturated water solutions of pristine SWNT (CNT$P$), and SWNT which have undergone sequential reactions on the same SWNT aliquot, CNT$R_1$, CNT$R_3$, and CNT$R_5$ correspond to the first, third and fifth consecutive reaction on the same batch of SWNT. After each reaction, an increase in SWNT solubility in water was observed. Furthermore, an increase in solubility



(a) Grind to fine powder 20 mg of SWNT + 1 g of peroxide
(b) Heat at 110 °C for 3-4 mins
(c) Add acetone (20 ml), sonicate 1 min
(d) Centrifuge mixture, decant supernatant and repeat step (c) once with acteone and once with water
(e) Allow to dry and collect powder (or can filter using 0.2 μm PTFE filter)

**Scheme 1** Carboxylic acid functionalisation of SWNT.

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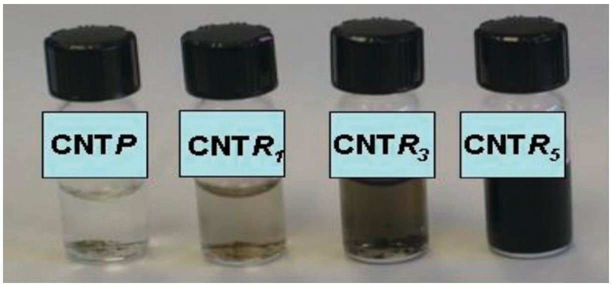

**Fig. 1** Photograph of vials containing pristine (CNT*P*) and carboxylic modified (CNT$R_1$–CNT$R_5$) SWNT in water at pH 9. $R_1$, $R_3$, and $R_5$ correspond to the first, third and fifth consecutive reaction on the same batch of SWNT, respectively. All samples are saturated solutions prepared by sonication for 15 min of 1 mg of SWNT in 1 ml $H_2O$ (pH 9), followed by centrifugation to remove undissolved SWNTs.

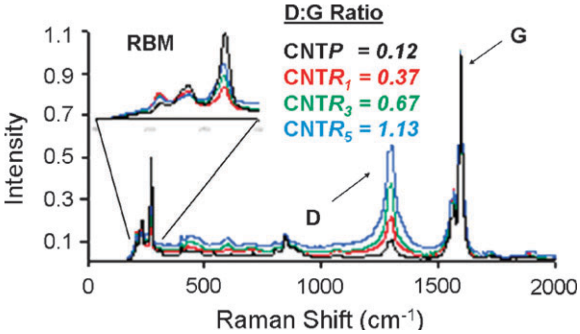

**Fig. 3** Resonant Raman spectra (785 nm excitation) of CNTP (black line), CNT$R_1$ (red line), CNT$R_3$ (green line) and CNT$R_5$ (blue line).

was found at higher pH's, direct evidence of the presence of acidic groups.

Optical absorption spectra (Fig. 2) show a dampening of the van Hove singularities after functionalisation suggesting that the functionalisation happened on the sidewalls of the SWNT.[13] Resonant Raman spectroscopy (Fig. 3) shows a change in the D to G ratio after all the sequential reactions. The ratio increases approximately linearly, suggesting that the extent of the reaction is roughly controllable. Fig. 4 shows an atomic force microscopy (AFM) image of well dispersed functionalized carbon nanotubes to show the ease of dispersion that can be achieved through our synthetic method.

The extent of functionalisation was determined by thermogravimetric analysis (TGA, Fig. 2: inset).[12] 64% of the final weight remains after heating to 600 °C, accounting for one in twelve carbons being modified,[11] double what has previously been published in the literature for this reaction.[12]

In order to highlight the usefulness of the –COOH functionalised SWNT, we carried out an amide coupling reaction with dodecylamine (DDA). CNT$R_5$ (2 mg) was sonicated then heated to 80 °C in thionylchloride (10 ml) for 24 h to activate the carboxylic acid group. This was then reduced to a black solid under vacuum and a solution of DDA (1 g in 10 ml THF) was added. This mixture was sonicated, heated to 40 °C overnight, filtered, then washed with 200 ml THF and dried. As expected, the final product was insoluble in water but soluble in deuterated chloroform after sonication. Fig. 5 shows the $^1$H NMR of DDA in solution and on the surface of the SWNT. The broadening of the peaks indicates that the DDA molecule is on the surface of the SWNT. Also of note is the large shift in the α and β protons adjacent to the amide, probably due to a large SWNT desheilding effect.

The carboxylic acid reaction addresses a problem with current functionalisation techniques. Most reactions depend on the ability to disperse pristine SWNT in a solvent. This generally requires large solvent to nanotube ratios (*e.g.*, 20 mg in 200 ml). Dispersion is achieved by long and costly sonication to break up SWNT bundles so as to expose the maximum amount of SWNT surface for the reaction. However, it has been shown that extended periods of sonication can damage the nanotube structure.[14] More importantly, due to the large ratios of SWNT to solvent these procedures are not easily scalable for potential commercial applications. The removal of the solvent from the reaction creates an intrinsically scalable process.

In conclusion, an ultra-fast method for functionalising the sidewall of SWNT with a carboxylic acid moiety has been

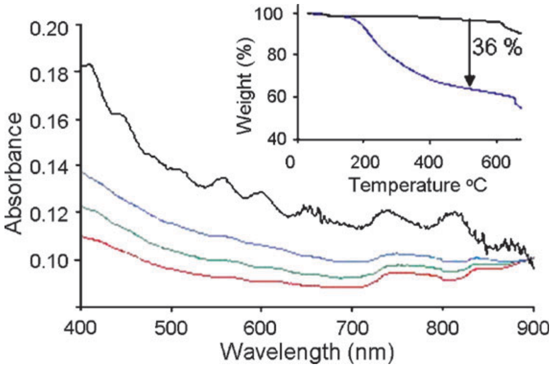

**Fig. 2** Optical absorption spectra for CNT*P* (black line), CNT$R_1$ (red line), CNT$R_2$ (green line) and CNT$R_3$ (blue line). The solvent for the pristine sample was 1-methyl-pyrolydone and that for the carboxylic acid products was water. Inset: TGA of pristine (black line) and CNT$R_5$ (blue line).

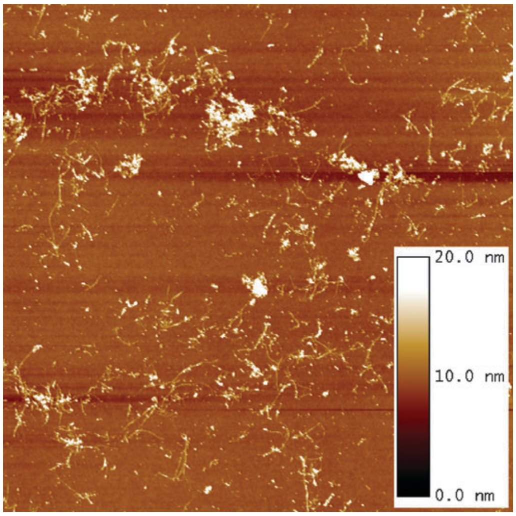

**Fig. 4** AFM of CNT$R_5$ cast on Si slides showing highly dispersed COOH functionalised SWNT. The image is 10 μm by 10 μm, the inset shows the height scale.

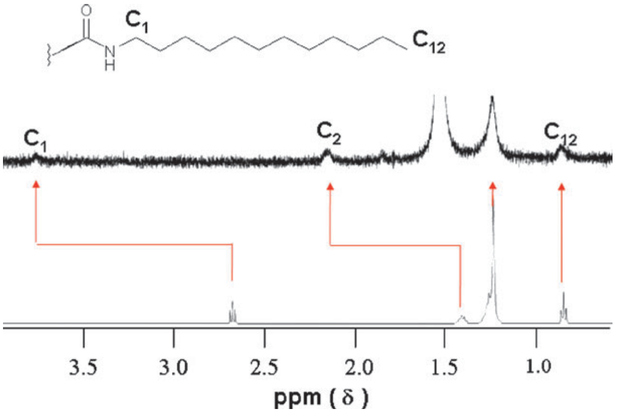

**Fig. 5** $^1$H NMR of DDA (structure shown on top when bound to a SWNT) before (bottom) and after (top) reaction with SWNT. Both spectra were recorded in $CDCl_3$.

presented. The method does not require the use of any solvent, hence it is readily scalable. Also, control over the amount of functionalisation has been achieved. The final product is water soluble and can undergo amide bond formation to potentially attach a variety of functional groups to the nanotubes.

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