Functionalisation of carbon nanohorns†

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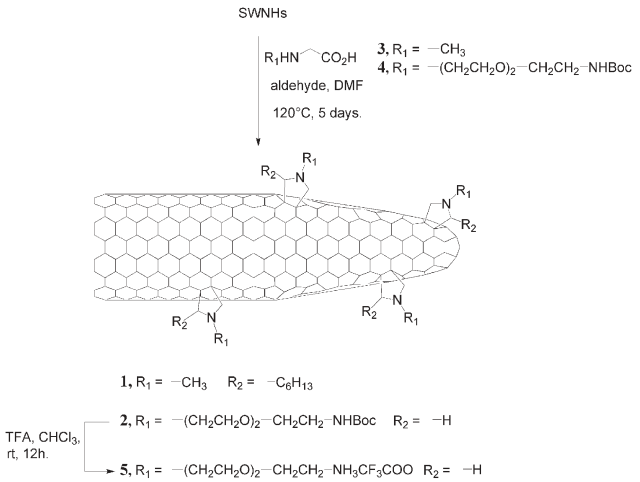
The functionalisation of single wall carbon nanohorns *via* 1,3-dipolar cycloaddition has been achieved, and the products have been characterised by spectroscopy, microscopy and thermogravimetry.

Nanometre-scale structures are under active investigation for producing innovative materials, composites, and electronic devices of greatly reduced size. Single wall carbon nanohorns (SWNHs) are a new class of carbon-based nanomaterials derived from SWNTs. Discovered by Iijima *et al.* in 1999,[1] SWNHs are typically composed of a tube of about 2–5 nm in diameter and 30 to 50 nm long, closed by a cone at one extremity. SWNHs associate with each other to give rise to round-shaped aggregates of 100 nm in diameter. Their large surface areas and porosity ensure a great affinity with organic compounds[2–4] and make them promising candidates for hydrogen and methane storage[5–8] as well as drug delivery systems.[9,10]

The organic functionalisation of SWNHs may open new doors for the use of nanohorns in materials science and may also increase their solubility in water in view of biomedical applications. A few years ago, we demonstrated that the functionalisation of carbon nanotubes[11,12] *via* 1,3-dipolar cycloaddition[13] allows an increase in their solubility in organic solvents as well as their processing ability.[14] Herein, we describe the functionalisation and characterisation of single wall nanohorns. The nanohorns were produced with a high purity by electric arc ablation of graphite by Nanocraft, Inc. (www.nanocraftinc.com).

Compounds **1** and **2** (Scheme 1) were obtained by reaction between the pristine nanohorns and the suitable aldehyde and amino acid in DMF (heptanal and **3** for **1** and amino acid **4**[15] and paraformaldehyde for **2**). In a typical experiment, SWNHs (80 mg) were dispersed in DMF (100 ml), heptanal (0.300 ml) and sarcosine (750 mg) were added in portions (0.1 ml of heptanal and 250 mg of sarcosine every 24 h) and the reaction mixture was heated at 130 °C for 4 days. After separation of the insoluble material by centrifugation, the solvent was removed and the resulting residue was diluted with chloroform and washed with water. The combined organic phases were dried and the solvent was evaporated. The residue was washed several times with THF to remove the by-products (until the solution was colorless) and then the black powder, obtained after centrifugation, was dried under vacuum affording **1** or **2** (10 mg and 4.4 mg in the respective



Scheme 1 Synthesis of the nanohorn derivatives **1**, **2** and **5**.

reactions). After reaction, the functionalised nanohorns were soluble in DMF (0.25 mg ml^{-1} for **1** and 0.1 mg ml^{-1} for **2**), chloroform (0.4 mg ml^{-1} for **1** and 0.2 mg ml^{-1} for **2**) and dichloromethane (0.4 mg ml^{-1} for **1** and 0.1 mg ml^{-1} for **2**) (Fig. 1) but insoluble in THF, diethyl ether and methanol.

The *tert*-butoxycarbonyl (Boc) protecting group of compound **2** was removed by treatment of **2** with trifluoacetic acid (TFA) in chloroform. The corresponding nanohorns functionalised with ammonium triflate salt end group, **5**, precipitated during the acid treatment and were recovered by filtration over a 0.2 μm Millipore membrane and then washed extensively with chloroform and diethyl ether. The nanohorn derivative **5** was found to be partially soluble in water and in methanol. To improve the solubility in such polar solvents, the length of the ethylene glycol chain needs to be increased.

Fig. 1 Pristine SWNHs in chloroform (left) and nanohorns **1** in chloroform (middle) and in DMF (right).

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The nanohorn derivatives were characterised by Raman and UV-Vis spectroscopies as well as electron microscopy and thermogravimetry. The Raman spectrum of pristine SWNHs shows characteristic features with a very intense D band, comparable or more intense than the G band.[16] The D band also shows a characteristic dispersion since it is found at 1350 cm^{-1} exciting at 488 nm and at 1325 cm^{-1} exciting at 633 nm. In Fig. 2 the spectra are normalised to the peak intensity of the G band after subtraction of the background from the spectra of SWNHs **2**. The comparison shows that for functionalised SWNHs there is some lowering of the relative intensity of the D bands and this might indicate that the reaction helps in decreasing the number of defects present in SWNHs, probably by removing some of the amorphous impurities.[17]

The UV-Vis spectra of the pristine nanohorns present two maxima at 227 and 276 nm. The spectra of functionalised nanohorns **1** and **2** exhibit a broad absorption around 250 nm with a shoulder around 300 nm, which monotonically decreases in intensity until the near IR region (Fig. S1†).

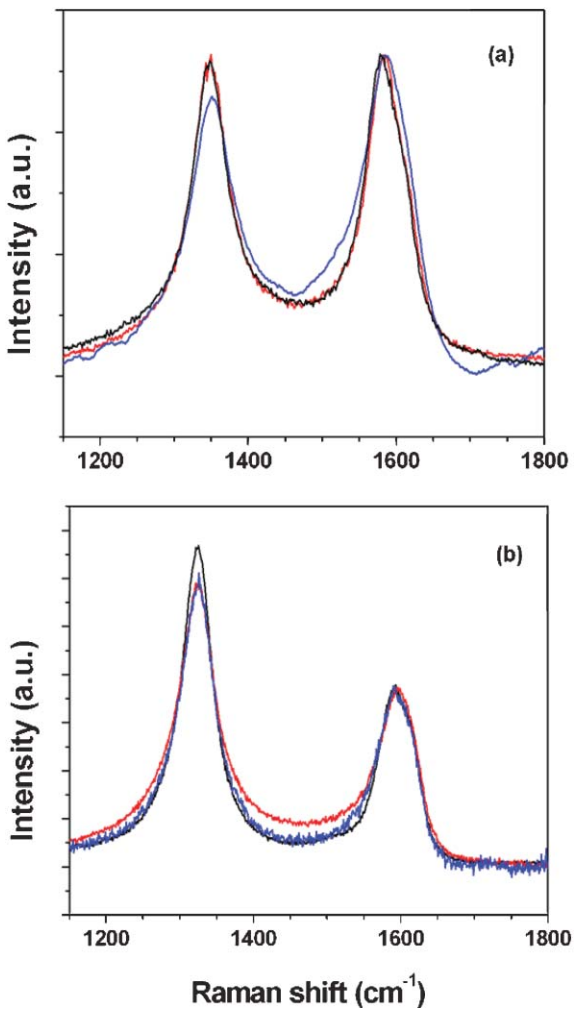

Fig. 2 Raman spectra of SWNHs using exciting line at 488 nm (a) and 633 nm (b). Pristine SWNHs (black line), SWNHs **1** (red line), SWNHs **2** (blue line). The bands are normalised to the peak intensity of the G band and the background was subtracted from the spectrum of SWNHs **2** to better compare D and G bands.

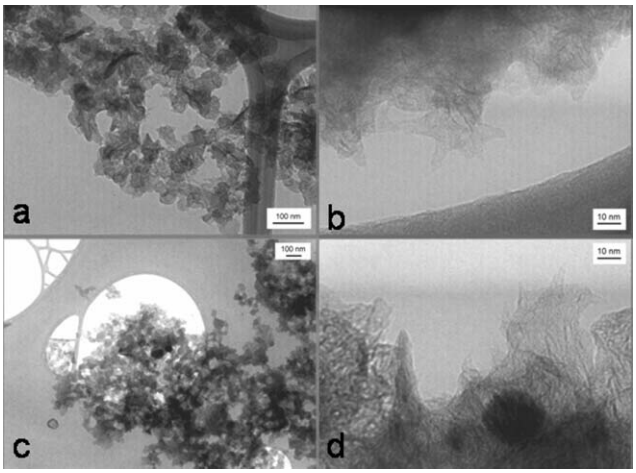

Fig. 3 TEM images of the pristine SWNHs (a) and (b) and of the nanohorn derivative **1** (c) and (d). The scale bars represent 100 nm in pictures (a) and (c) and 10 nm in pictures (b) and (d).

Compounds **1** and **2** as well as the pristine material were investigated by transmission and scanning electron microscopy (SEM, TEM). The TEM pictures of all the compounds revealed the presence of nanohorns. The images consist of small aggregates of nanohorns (round-shaped aggregates with a diameter of about 100 nm) in which it is possible to distinguish small conical caps pointing out (Fig. 3). Almost no difference can be noticed between the pristine material and the functionalised nanohorns.

For the SEM analysis, the samples were dissolved in DMF and a drop was deposited on a glass substrate. After drying, the glass slides were covered by gold. The SEM pictures are in agreement with the TEM observations, showing the presence of round-shaped nanohorn aggregates of about 100 nm of diameter (Fig. 4 and Fig. S2†).

Comparison between the pristine and the functionalised nanohorns shows very similar materials, though a better dispersion on the surface is observed in the case of the functionalised nanohorns.

The covalent functionalisation of the nanohorns was confirmed by thermogravimetric analysis (TGA). The pristine nanohorns are very stable, showing a very low degree of degradation up to 800 °C under nitrogen. The loss of weight which corresponds to the loss of the organic groups present on the nanohorns relative to the pristine nanohorns is ~19% for nanohorn **1** at 600 °C (Fig. 5), which would correspond to about one pyrrolidine group every fifty carbon atoms. Attention must be paid to the noncovalent attachment to the nanohorns. Similar to other forms of carbon, such as active carbon or carbon nanotubes, many organic substances stick to the surface of nanohorns. We have found that DMF tends to adsorb to the nanohorns. Therefore, prior to analysis, the functionalised nanohorns were left under vacuum at room temperature overnight.

The nanohorns are not de-aggregated during the reaction. The round-shaped aggregates remain intact in solution and are functionalised only on the periphery because of the reactivity of the cap of the nanohorns and also because of the accessibility. SWNHs seem to be promising for drug delivery; the covalent attachment of bioactive moieties for targeting cells or organs appears to be the next step towards applications of such materials.

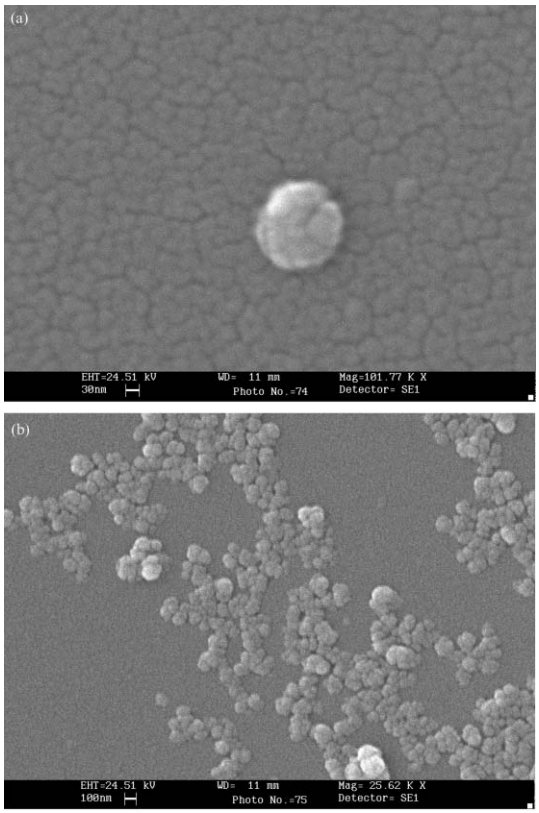

Fig. 4 SEM images of the functionalised nanohorns **1**. The scale bar represents 100 nm (top) and 30 nm (bottom).

In conclusion, we have described the functionalisation of single wall nanohorns *via* 1,3 dipolar cycloaddition. The nanohorn derivatives present a good solubility in common organic solvents. The TEM and SEM images show that the nanohorns are aggregated forming characteristic secondary nanostructures. The functionalisation of nanohorns is still under investigation with the major goal to isolate single or small aggregates of nanohorns and to determine their optical, photophysical and electrochemical properties.

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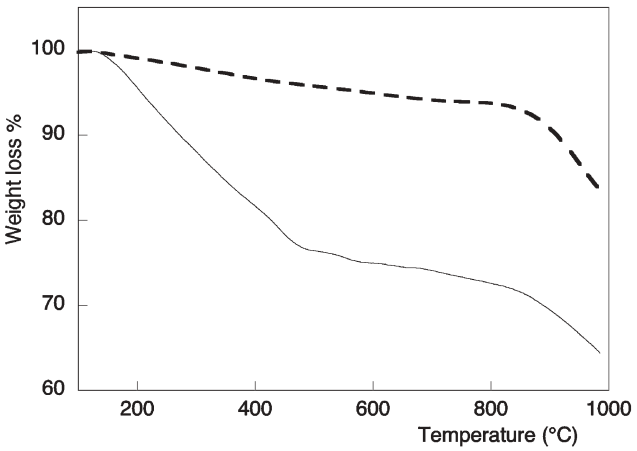

Fig. 5 Thermogravimetric analysis (N_2, 10 °C min^{-1}) of the pristine SWNHs (dashed line) and SWNHs **1** (solid line).

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