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Sidewall modification of single-walled carbon nanotubes using photolysis of perfluoroazooctane†

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Photolysis of perfluoroazooctane with single-walled carbon nanotubes led to sidewall modification of the surface with the introduction of perfluorooctyl functional groups, confirmed by means of Raman, XPS, FT-IR, mass, UV-vis-NIR and SEM measurements.

Carbon nanotubes[1] (CNTs) are very attractive for a wide range applications because of their unique electronic, optical and mechanical properties.[2,3] Single-walled carbon nanotubes (SWNTs) possess high Young's modulus[4] and can be metallic or semiconducting, depending on diameter and helicity. Sidewall modifications of CNTs have been expected to lead to improvements in their original behavior. We can find recent studies on the introduction of organic functional groups on the surface of CNTs by using photo- and thermochemical methods. Since CNTs are not soluble in organic solvents and water, oxygenated CNTs possessing carboxy acid moieties were used as starting materials for the sidewall functionalizations in most of these studies,[5] while there have been few reports on direct reactions to sidewall carbon atoms of CNTs.[6]

On the other hand, perfluoroalkyl-containing materials have attracted much attention because of their unique properties derived from the presence of fluorine atoms.[7] Previously we reported that photolysis of perfluoroazooctane (**1**) gave perfluorooctyl radicals effectively in solution under mild conditions for perfluoroalkylation of organic compounds.[8] Introduction of substituents containing fluorine atoms would result in improvement of the original behavior of CNTs. To date, chemical modification of CNTs surfaces with fluorine and fluoro-containing substituents has been studied by use of F_2 gas,[9] CF_4 plasma[10] and perfluoroalkyl iodide.[11] These methods would cause problems in the handling of the reactions and in the formation of undesired by-products during the reaction, and make it necessary to use special vessels. In this paper, we report on a useful method for sidewall modification of SWNTs with perfluoroalkyl substituent by using photolysis of **1**.

A typical experiment is described as follows. Azo compound **1** (3 mg), prepared according to the literature,[12] in perfluorohexane (4 ml) was irradiated with a low-pressure mercury lamp for 8 h at room temperature in the presence of purified SWNTs (5 mg, 0.9–1.2 nm diameter, 10–50 μm length) purchased from Aldrich Co. Inc. and an argon atmosphere with stirring. After removal of the perfluorohexane solution from the reaction mixture, the residual powders were washed with perfluorohexane and hexane. The obtained powders were analyzed with SEM, Raman, X-ray photoelectron, diffuse reflectance infrared Fourier transform (DRIFT), mass and UV-vis-NIR spectrometers.

Fig. 1 shows Raman spectra of SWNTs, in pristine condition and after perfluorooctylation. Characteristic peaks at 180, 165 and 149 cm^{-1} were observed due to a breathing mode of SWNTs. In the case of functionalized SWNTs, the breathing mode is suppressed by introduction of the perfluorooctyl substituent. Typical peaks were also shown at 1592 and 1342 cm^{-1} attributed to G and D bands, respectively. The peak intensity of the D band in functionalized SWNTs increased in comparison with pristine SWNTs, showing the presence of scattering defects on the sidewall of SWNTs due to covalent functionalization.

XPS spectra of the SWNTs were measured before and after perfluorooctylation treatment (Fig. 2), and showed the formation after irradiation of a new peak at 687.6 eV of fluorine 1s together with an sp^2 carbon peak at 284.1 eV . In the carbon 1s region, a peak at 290.9 eV with higher binding energy compared with untreated CNTs was ascribed to carbon atom bound to fluorine atom.

Fig. 3 shows the IR spectrum of the SWNTs sample after treatment with **1** upon irradiation. A new peak was observed at 1050–1270 cm^{-1} with C–F stretching band accompanied with C=C bond peak (1630 cm^{-1}), as contrasted with no peaks in the case of pristine SWNTs consistent with a previous report.[13] These results suggest that perfluorooctyl radicals generated by photolysis of **1** with elimination of nitrogen, reacted with C=C bond on the SWNTs

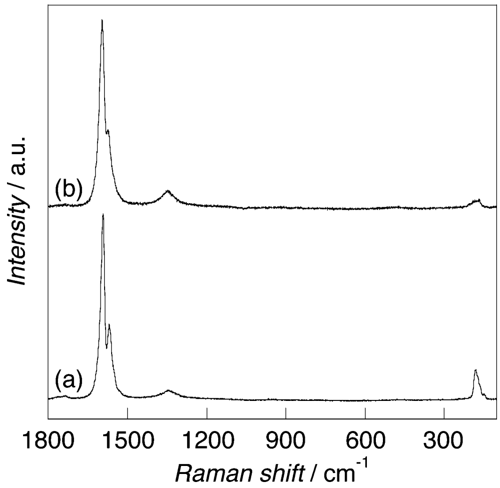

Fig. 1 Raman spectra (514.4 nm) of (a) pristine and (b) functionalized SWNTs with perfluorooctyl substituent.

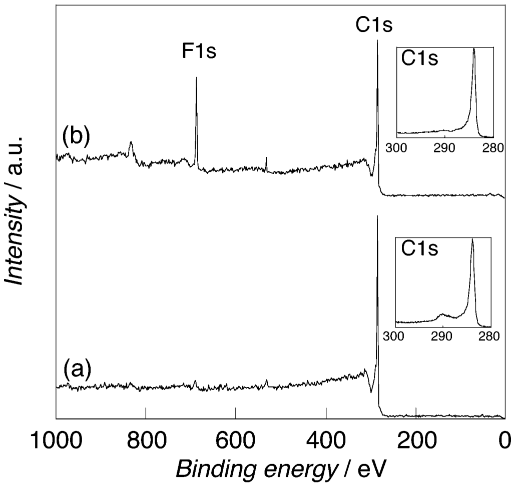

Fig. 2 XPS spectra of SWNTs (a) before and (b) after irradiation with perfluoroazooctane (**1**). The inset is carbon 1s spectra.

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† Electronic supplementary information (ESI) available: Fig. S1. UV-vis-NIR spectra of pristine and modified SWNTs. See http://www.rsc.org/suppdata/cc/b4/b402206h/

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sidewall (Scheme 1). This method is useful for introduction of perfluorooctyl functionality on the sidewall of SWNTs, since nitrogen formed by photolysis of **1** is inert to both SWNTs and functionalized SWNTs and no undesired by-products are formed.

In order to confirm the introduction of the perfluorooctyl moiety on the sidewall of SWNTs, components generated by heating functionalized SWNTs to 300 °C were analyzed with mass spectroscopy (Fig. 4). The spectrum shows a parent peak at *m*/*z* 419 ($C_8F_{17}^+$) ascribed to the perfluorooctyl group with fragmentation peaks *m*/*z* 219 ($C_4F_9^+$), 181 ($C_4F_7^+$), 169 ($C_3F_7^+$), 131 ($C_3F_5^+$), 119 ($C_2F_5^+$), 100 ($C_2F_4^+$) and 69 (CF_3^+), consistent with C_8F_{17} moiety.

Moreover, UV-vis-NIR spectra of pristine and modified SWNTs were measured in DMF (see ESI, Fig. S1†). Excess of sidewall modification on the surface of CNTs would result in changes to their original electronic behavior. The comparison of spectra between pristine and modified SWNTs indicates that sidewall functionalization of SWNTs with perfluorooctyl substituent maintains the original electronic structure of SWNTs without heavy modification.[11] As shown in Fig. 5, the SEM image of modified SWNTs with perfluorooctyl functional group reveals no significant changes after introduction of the substituent, compared with that of pristine SWNTs.[10] The similar bundle structures of modified SWNTs with pristine SWNTs would be due to there being only a small amount of fluorine functionality introduced on sidewall SWNTs derived from no heavy modification.

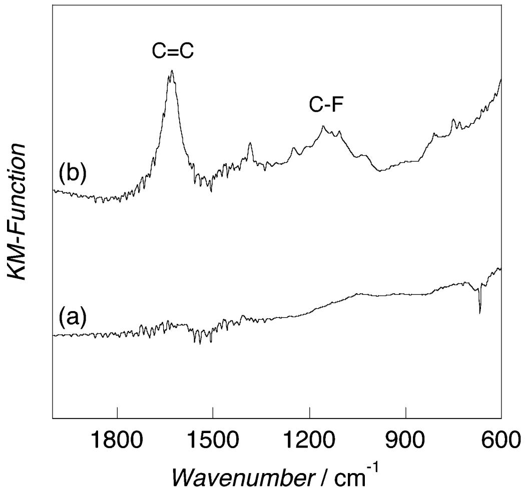
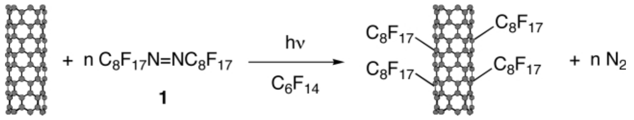


Fig. 3 IR spectra of (a) untreated SWNTs and (b) SWNTs after treatment of perfluorooctylation.



Scheme 1

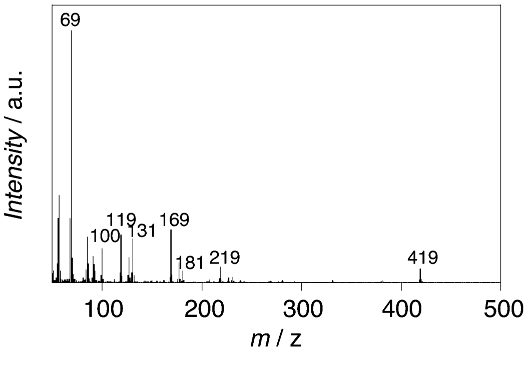


Fig. 4 Mass spectra of perfluorooctylated SWNTs after heating to 300 °C.

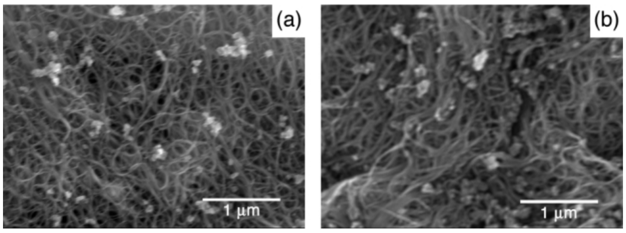


Fig. 5 SEM images of (a) untreated and (b) perfluorooctylated SWNTs.

Photolysis of azo compound **1** with SWNTs led to sidewall modification of the surface with perfluorooctyl functional groups. The introduction of the perfluoroalkyl substituent was confirmed by means of Raman, XPS, FT-IR, mass and UV-vis-NIR measurements. This method is useful for modification of sidewall SWNTs with the perfluorooctyl moiety since no by-products are formed and there is no destruction of SWNTs electronic behavior from heavy modification. Precise investigations to determine the position of the fluorine moieties on sidewall and tube end of SWNTs are under investigation.

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