Sidewall Modification of Single-walled Carbon Nanotubes with Sulfur-containing Functionalities and Gold Nanoparticle Attachment

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Photolysis of cyclic disulfides with single-walled carbon nanotubes led to a sidewall modification of the surfaces to introduce sulfur-containing functional groups, as confirmed by means of Raman, XPS, FT-IR, mass, and UV–vis–NIR measurements. A subsequent treatment of sulfur-containing substituents modified SWNTs with gold nanoparticles gave an attachment of gold on the surface of SWNTs through thioalkylthiol linkage.

Single-walled carbon nanotubes (SWNTs) have much attracted to a wide range application using their unique electronic, optical, and mechanical properties[1,2] derived from their high Young modulus[3] and metallic or semiconducting properties depending on diameter and helicity. Sidewall modifications of SWNTs have been expected to lead to improvement of its original behavior. We can find recent studies on introduction of organic functional groups on the surface of SWNTs by using photo- and thermochemical methods. Since SWNTs are not soluble in organic solvents and water, oxygenated SWNTs possessing carboxyl acid moieties were used as starting materials for sidewall functionalizations in most studies,[4] meaning that these methods give rise to many defects due to heavy modification on the surface of SWNTs.

Sulfur-containing materials have attracted much attention because of their unique properties derived from the presence of sulfur atoms.[5] Especially, it is well-known that organic compounds containing thio and thiol groups show good affinities with gold to give self-assembled monolayer. To date, chemical modification of SWNTs surfaces with sulfur-containing substituents has been studied by use of H_2S gas with ball-milling method[6] and of further functionalization process of carboxylated SWNTs treated with thionyl chloride.[7] These methods would make problems about handling of the reactions and about multistep reaction and make it necessary to use special vessels. Previously, we reported that chemical modification of SWNTs with fluorine functionalities by use of radical reactions, which took place under mild conditions and gave no heavy modification[8] compared with conventional methods described above.[4] It is known that cyclic disulfides are photolysed easily to give α,ω-alkyldithio radicals.[9] In this paper, we report on a useful method for sidewall modification of SWNTs with sulfur-containing substituents by using a radical process of photolysis of cyclic disulfides **1**.

Typical experiments are described as follows: Cyclic disulfides **1** (2 mg), prepared according to the literature,[10] in acetonitrile (4 mL) were irradiated with a 60-W low-pressure mercury lamp (Eikosha EL-S-SQ-60) with a UV cut filter (<200 nm) for 4 h at room temperature in the presence of purified SWNTs (5 mg, 0.9–1.2-nm diameter, 10–50-µm length) in an argon atmosphere with stirring. After removal of acetonitrile from the reaction mixture, the residual powders were washed with acetonitrile. The obtained powders were analyzed by DRIFT, XPS, SEM, Raman (514.5 nm), and UV–vis–NIR spectrometers. An attachment of gold nanoparticles on the surface of thioalkylthiolated SWNTs was carried out from mixture of the modified SWNTs (1.7 mg) and gold colloid (5 mL), prepared according to the literature,[11] with stirring overnight. After finishing the reaction, the aqueous solution was removed from the reaction mixture, then washed with water.

Figure 1a shows Raman spectra of pristine and treated SWNTs upon irradiation with cyclic disulfide **1a**. Characteristic peaks at 180, 165, and 149 $\mathrm{cm^{-1}}$ due to a breathing mode of SWNTs were observed. In the case of functionalized SWNTs, the breathing mode is suppressed by introduction of sulfur-containing substituents. Typical peaks were also shown at 1592 and 1342 $\mathrm{cm^{-1}}$ attributed to G and D band, respectively. The peak intensity of D band in functionalized SWNTs increased in comparison with pristine SWNTs, showing the presence of scattering defects due to covalent functionalization on sidewall of SWNTs.

XPS spectra of SWNTs were measured before and after treatment of thioalkylthiolation with cyclic disulfide **1a** (Figure 1b(i, ii)), indicating that a new peak at 163.7 eV of sulfur 2p together with sp^2 carbon peak at 284.6 eV was observed after irradiation. In the carbon 1s region, the carbon peak became broad owing to mixture of sp^2 carbon and carbon atom bound to sulfur atom with higher binding energy compared with untreated SWNTs. Photolysis of cyclic disulfides **1b** and **1c** took place the similar reaction with SWNTs to give surface modification with sulfur moieties. From XPS analyses, sulfur/carbon area ratios were estimated to be 0.13, 0.11, and 0.10 by use of **1a**, **1b,** and **1c**, respectively, upon irradiation for 4 h.

Furthermore, an attachment of gold nanoparticles to sulfur-functionalized SWNTs was investigated. As shown in Figure 1b(iii), the XPS spectrum after treatment of sulfur-functionalized SWNTs formed by photoreaction of SWNTs and **1a**

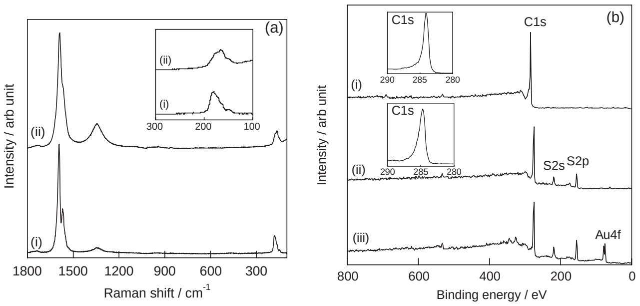


Figure 1. (a) Raman spectra of (i) pristine and (ii) functionalized SWNTs with sulfur-containing substituent. (b) XPS spectra of SWNTs (i) before and (ii) after irradiation with cyclic disulfide **1a**. (iii) XPS spectrum of sulfur-functionalized SWNTs after treatment with gold nanoparticles.

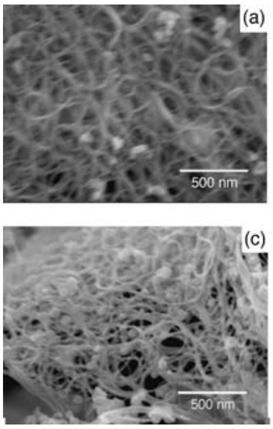


Figure 2. SEM images of (a) untreated, (b) sulfur-functionalized SWNTs, and (c) gold nanoparticle-assembled sulfur-functionalized SWNTs.

with gold colloid[11] shows a new peak at 84.2 eV of gold 4f together with sp^2 carbon peak at 284.6 eV and sulfur peak at 163.7 eV. As shown in Figures 2a and 2b, the SEM image of modified SWNTs with sulfur-containing functional group reveals no significant changes after introduction of the substituent compared with that of pristine SWNTs,[10] and then gold nanoparticles self-assembly to sulfur moieties on the surface of SWNTs was observed in Figure 2c.

IR spectra of the SWNTs sample before and after treatment of irradiation with **1a** are shown in Figure 3a. A new peak was observed at 2914 and 2838 cm^{-1} with C–H stretching band attributed to methylene group of $–S(CH_2)_4SH$, accompanied with C=C bond peak (1573 cm^{-1}), as contrasted with no peaks in the case of pristine SWNTs. These results suggest that in α,ω-dithio radical generated by photolysis of **1**, thio radical reacted with C=C bond on SWNTs sidewall, and the other one abstracted hydrogen from acetonitrile as a solvent to give thioalkylthiolated SWNTs (Scheme 1). This method is useful for introduction of sulfur-containing functionalities on sidewall of SWNTs.

In order to confirm the introduction of sulfur-containing moieties on sidewall of SWNTs, components generated by heating sulfur-functionalized SWNTs after treatment with **1a** to 300 °C were analyzed by mass spectroscopy (Figure 3b). The spectrum shows a parent peak at m/z 119 ($C_4H_7S_2^+$) ascribed to thiobutylthiol group with fragmentation peaks m/z 87 ($C_4H_7S^+$), 73 ($C_3H_5S^+$), 67 ($C_5H_7^+$), 64 (S_2^+), 60 ($C_2H_4S^+$), 55 ($C_4H_7^+$), 45 (CHS^+), and 41 ($C_3H_5^+$) consistent with $–S(CH_2)_4SH$ moiety.

Moreover, UV–vis–NIR spectra of pristine and modified SWNTs were measured in DMF as shown in Supporting Information. Excessive sidewall modification on the surface of CNTs would result in changes their original electronic behavior. The comparison of spectra between pristine and modified SWNTs indicates that sidewall functionalization of SWNTs with sulfur-containing substituents maintains original electronic structure of SWNTs without heavy modification.[12]

In conclusion, photolysis of cyclic disulfides **1** with SWNTs led to a sidewall modification of the surface to form sulfur-containing functional groups. The modified SWNTs with sulfur-containing functionalities is applicable to an attachment with gold nanoparticles on sidewall SWNTs. This method is useful for modification of sidewall SWNTs with sulfur-containing moieties because of no formation of byproducts and no destruction of SWNTs electronic behavior by heavy modification.

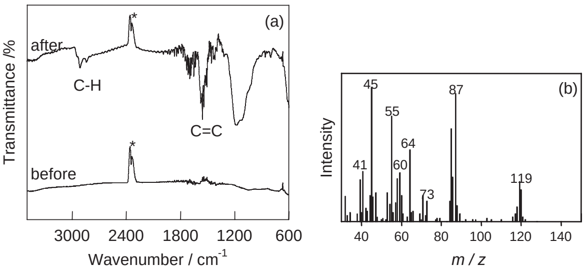
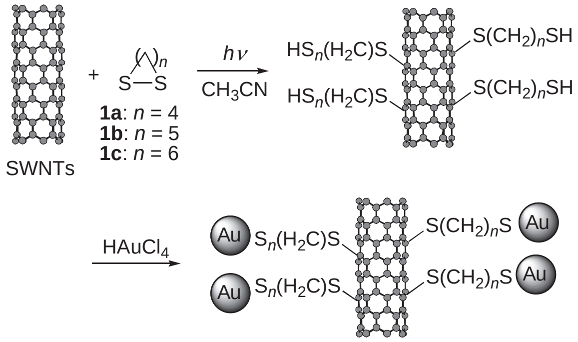


Figure 3. (a) IR spectra of untreated SWNTs and SWNTs after treatment of thioalkylthiolation with **1a**. (b) Mass spectrum of sulfur-functionalized SWNTs with **1a** after heating to 300 °C.



Scheme 1. Chemical modification of SWNTs with cyclic disulfides **1** and subsequent treatment with Au nanoparticles.

References

1 M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerene and Carbon Nanotubes*, Academic Press, San Diego, **1996**.
2 R. Saito, M. S. Dresselhaus, G. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, **1998**.
3 A. Zettl, *Adsorbent Carbon Workshop and Science of Carbon Nanotubes Workshop*, Lexington, **1997**.
4 T. Lin, V. Bajpai, T. Ji, L. M. Dai, *Aust. J. Chem.* **2003**, *56*, 635, and references are there in.
5 P. Philip, *Organosulfur Chemistry*, Academic Press, London, **1995**.
6 Z. Konya, *Chem. Phys. Lett.* **2002**, *360*, 429.
7 J. K. Lim, *Synth. Met.* **2003**, *139*, 521.
8 T. Nakamura, M. Ishihara, T. Ohana, A. Tanaka, Y. Koga, *Chem. Commun.* **2004**, 1336.
9 V. Ramakrishnan, S. D. Thompson, S. P. McGlynn, *Photochem. Photobiol.* **1965**, 907.
10 M. H. Ali, M. McDermott, *Tetrahedron Lett.* **2002**, *43*, 6271.
11 K. R. Brown, D. G. Walter, M. J. Natan, *Chem. Mater.* **2000**, *12*, 306.
12 K. A. Park, Y. S. Choi, Y. H. Lee, C. Kim, *Phys. Rev. B* **2003**, *68*, 045429.

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