



Self-assembly of gold nanoparticles to carbon nanotubes using a thiol-terminated pyrene as interlinker

Luqi Liu ^{a,1}, Tongxin Wang ^{a,1}, Junxin Li ^{a,1}, Zhi-Xin Guo ^{a,*},
Liming Dai ^{a,b,2}, Deqing Zhang ^a, Daoben Zhu ^a

^a *Institutes of Chemistry, Center for Molecular Sciences, Chinese Academy of Sciences, Beijing 100080, China*

^b *Department of Polymer Engineering, The University of Akron, 250 South Forge Street, Akron, OH 44325-0301, USA*

Received 16 September 2002

Abstract

Gold nanoparticles were self-assembled onto the surface of solubilized carbon nanotubes through an interlinker of bi-functionalized molecule (PHT) terminated with pyrenyl unit at one end and thiol group at the other end. While the fluorescence of PHT is quenched moderately by the carbon nanotubes, the fluorescence is almost totally quenched by the further binding of gold nanoparticles. The enhancement of the Raman responses of nanotubes by the gold nanoparticles is also observed. These results imply there are charge transfer interactions between nanotubes and gold nanoparticles.

© 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Owing to their unique physical properties, carbon nanotubes have been continuously attracting strong interest from many areas of science and technology. Recent research has extended to the modification of carbon nanotubes through covalent and non-covalent methods [1,2]. For example, Haddon and co-workers [3] first synthesized solu-

bilized carbon nanotubes by the amidation reaction of long chain amine with carboxylic acid groups on the surface of nanotubes. Dai and co-workers [4] demonstrated that small molecule with abundant conjugated π electrons such as pyrene derivatives could be bound onto the surface of carbon nanotubes through non-covalent π - π interactions. On the other hand, carbon nanotubes are potentially excellent one-dimensional nanoscale materials which may be used to construct nanoelectronic devices. In this context, it is necessitous to link nanotubes together or with other functional species so as to implement their function. While functional groups could be bounded directly on the surface of carbon nanotubes through covalent or non-covalent methods [4–8],

* Corresponding author. Fax: +86-10-6255-9373.

E-mail addresses: gzhixin@infoc3.icas.ac.cn (Z.-X. Guo), ldai@uakron.edu (L. Dai).

¹ Graduate School of the Chinese Academy of Sciences.

² Also corresponding author.

different carbon nanotubes could also be interconnected through chemical functionalization [9]. However, to link the carbon nanotubes with other species through an interlinker is still a field in infancy.

In this Letter, we report our recent approach to link didecylamine modified solubilized multi-walled carbon nanotubes (*s*-MWNTs) [10] with

gold nanoparticles together using 17-(1-pyrenyl)-13-oxo-heptadecanethiol (PHT, Fig. 1) [11] as an interlinker. Being a bi-functionalized molecule, PHT can be bound to the surface of carbon nanotubes through π - π interaction between its pyrenyl unit in one end and the sidewall of carbon nanotubes. In the meantime, the terminated thiol group in the other end of PHT can

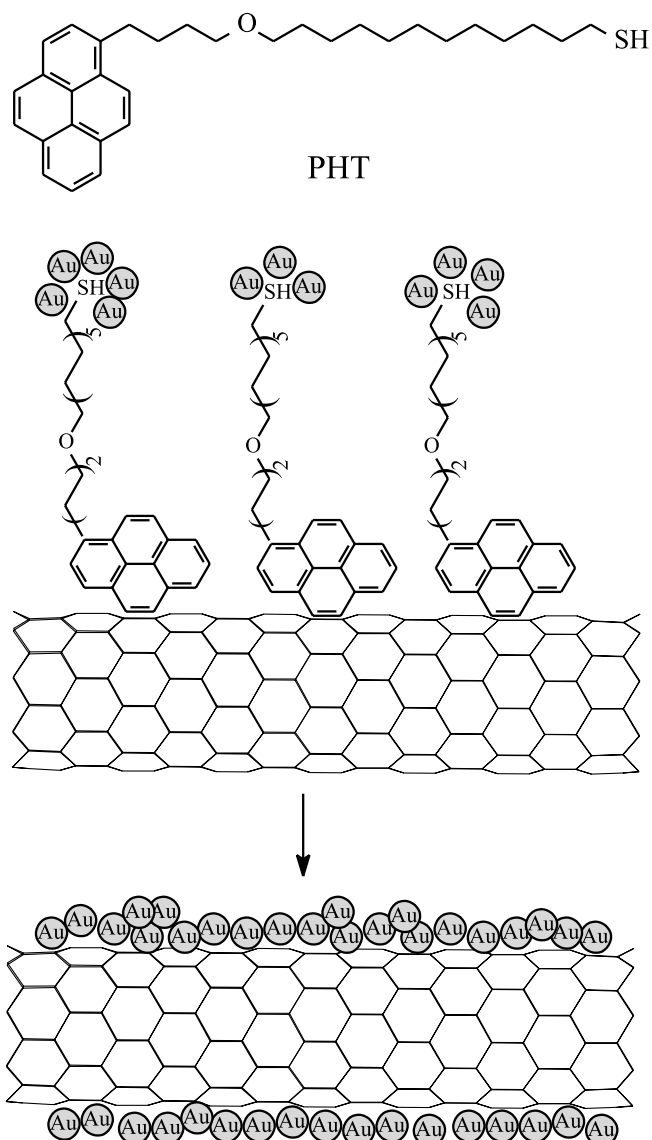


Fig. 1. The chemical structure of PHT and the illustration of the self-assembling process of gold nanoparticles with carbon nanotubes through PHT.

be bound to the surface of noble metal nanoparticles such as gold. Thus metal nanoparticles can be bound to the surface of carbon nanotubes through the interlinkage of PHT, just as shown in Fig. 1.

2. Experimental

The solubilized multi-walled carbon nanotubes (*s*-MWNTs) were obtained following the procedure reported before [10]. Briefly, the pristine multi-walled carbon nanotubes (MWNTs) were refluxed in concentrated nitric acid, then washed thoroughly with deionized water and dried completely. The resulting purified MWNTs (*p*-MWNTs) were converted to acylchloride in SOCl_2 and then reacted with didecylamine at 90–100 °C for 96 h. After removing the unreacted amine, the solubilized nanotubes were extracted into chloroform and filtered through a 0.2 μm PTFE membrane (Gelman). After removing the solvent, the final product (*s*-MWNTs) was obtained as a black solid. All of the other chemicals were used as received. The interlinker 17-(1-pyrenyl)-13-oxo-heptadecanethiol (PHT) was prepared and characterized according to published method [11].

In a typical experiment, 3 mg of PHT was incubated in a 10 ml solution of *s*-MWNTs in toluene (0.5 mg/ml). The mixture was sonicated for 30 min and then stood over 8 h at room temperature. The solution was concentrated to ca. 2 ml using a vacuum evaporator and then precipitated into 30 ml of ethanol. The precipitation was repeated until the ethanol solution was free from PHT which was monitored by UV–Vis absorption spectroscopy. The resulting solid was redissolved in 6 ml of toluene and was slowly added into 5 ml of gold colloid toluene solution (prepared according to Brust's method [12]) under nitrogen protection. After stirring at room temperature for 8 h, the mixture was concentrated to ca. 1 ml using a vacuum evaporator. The resulting solution was precipitated again into 20 ml of ethanol. After centrifuging, a dark brown solid was obtained, which could be dissolved again in toluene, obtaining a black solution.

Transmission electron microscopy (TEM) was performed on a PHILIPS TECNAI 20 instrument at 200 kV accelerating voltage. Linear transmittance spectra in the UV–Vis region were obtained using a computer-controlled Shimadzu UV-2501PC spectrophotometer. Raman spectroscopy was measured using Renishaw RM 2000 Microscopic confocal Raman Spectrometer at 632.8 nm (He–Ne laser).

Emission spectra were recorded on a Spex Fluorolog-3 photon-counting emission spectrometer equipped with a 450 W xenon lamp, a Spex 600 grooves/mm dual-grating (blazed at 1000 nm) as emission monochromator and 1200 grooves/mm grating (blazed at 600 nm) as excitation monochromator. The detector is a thermoelectronically cooled detector consists of a near-infrared-sensitive Hamamatsu R2658P photomultiplier tube operated at 1500 V. All of the experiments were done under room temperature. The emission spectra were uncorrected for the instrument response.

3. Results and discussion

The non-covalent binding of PHT on the surface of *s*-MWNTs can be observed from the absorption spectrum in toluene, which shows a typical featureless spectrum of solubilized carbon nanotubes with additional features of PHT at 345 and 328 nm, respectively (trace b, Fig. 2). As the mixture of *s*-MWNTs and PHT has been washed thoroughly to get rid of free PHT before redissolving in toluene, which was monitored by UV–Vis absorption spectroscopy, there should be no free PHT in the toluene solution. Thus the existence of the feature peaks of PHT strongly suggest the binding of PHT on the surface of *s*-MWNTs, most presumably through π – π interactions between the pyrenyl units of PHT and the sidewall of *s*-MWNTs [4]. As a result of π – π interactions [13], the absorption bands of PHT bound *s*-MWNTs become broader compared with that of pristine PHT (trace a, Fig. 2). The binding of gold nanoparticles through the thiol end of PHT can be clearly seen from the obvious typical surface plasmon band of gold nanoparticles centered at 523 nm (trace c, Fig. 2).

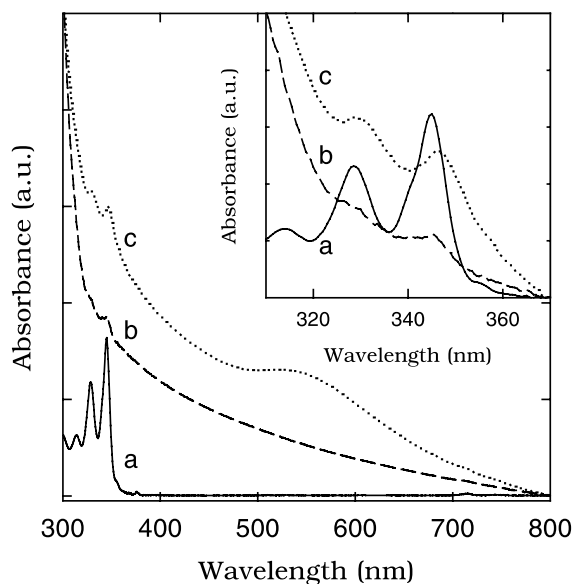


Fig. 2. The absorption spectra of PHT (trace a), *s*-MWNTs bound with PHT (trace b), and *s*-MWNTs bound with gold nanoparticles through PHT (trace c). The inset shows the corresponding enlarged spectra.

The TEM images give a direct vision of the gold nanoparticles immobilized *s*-MWNTs (Fig. 3). The *s*-MWNTs are densely coated with gold nanoparticles. The size distribution of gold nanoparticles is narrow, with an average particle size of ~ 5 nm. However, when the colloids of gold nanoparticles were mixed with *s*-MWNTs under the same condition without PHT, only few gold nanoparticles can be found on the nanotubes.

The fluorescence of the samples was also measured, respectively (Fig. 4). While the fluorescence of PHT is quenched moderately by the binding of *s*-MWNTs (trace b, Fig. 4), the emission of PHT is almost totally quenched through the further binding of gold nanoparticles (trace c, Fig. 4). This observation shows that the decay of singlet excited pyrene moieties is affected by its binding to *s*-MWNTs as well as gold nanoparticles. In order to gain a better understanding of the interaction between PHT and *s*-MWNTs at molecular level, we measured photoluminescence emission spectra of the PHT at different concentration of *s*-MWNTs in toluene solutions. Although the addition of *s*-MWNTs did not cause any new spectroscopic

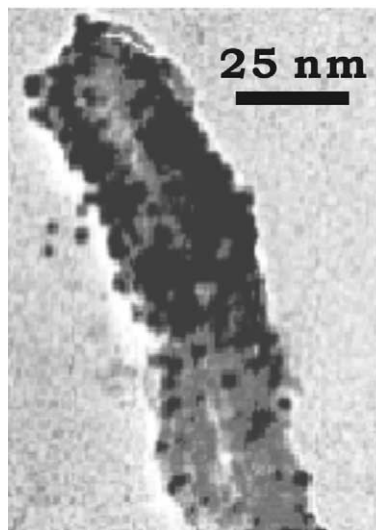


Fig. 3. TEM image of gold nanoparticles self-assembled on the surface of *s*-MWNTs through PHT.

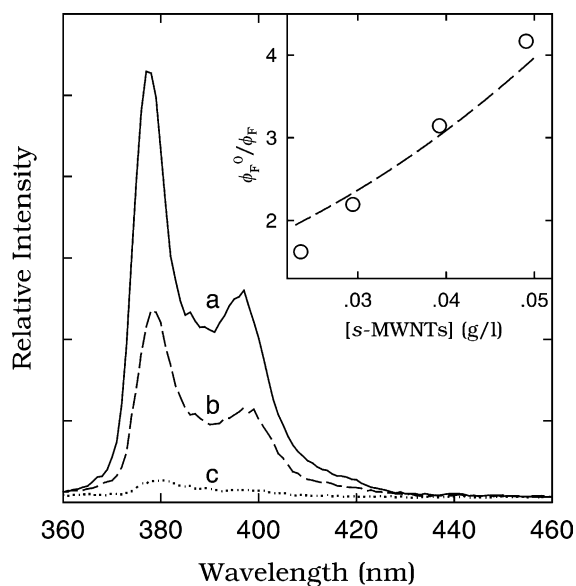


Fig. 4. The fluorescence spectra of PHT (trace a), *s*-MWNTs bound with PHT (trace b), and *s*-MWNTs bound with gold nanoparticles through PHT (trace c). The inset shows the Stern–Volmer curve plot for the quenching of photoluminescent intensities of PHT by *s*-MWNTs in toluene at room temperature (\circ). The line represents least squares fit.

feature, it did lead to a continuous decrease in the photoluminescence intensity at the peak position. By plotting the ratio of the photoluminescence

peak intensity without and with quencher, Φ_F^0/Φ_F , against the concentration of *s*-MWNTs, [*s*-MWNTs], a quenching curve with an upward curvature was obtained (inset of Fig. 4). The quenching curve is exponential, indicating the observed photoluminescence quenchings may be attributed to static quenching due to the formation of the ground state complexes and the excited state exciplexes [14,15]. The addition of gold nanoparticles quenches the fluorescence of PHT more efficiently, probably because of the energy transfer from PHT to gold nanoparticles [16].

The Raman spectrum of *s*-MWNTs (trace a, Fig. 5) shows a typical Raman spectrum of multi-walled carbon nanotubes made from CVD method [17,18]. After the binding of gold nanoparticles through PHT, the intensity of the corresponding Raman responses of *s*-MWNTs is increased (trace b, Fig. 5). Recently, the enhancement of Raman responses of carbon nanotubes through their absorbing on the surfaces of gold or silver was reported by several research groups [19–23]. There are two major contributions to the surface enhancement of Raman scattering of carbon nanotubes on metallic surfaces: the ‘electromagnetic’

mechanism and the ‘chemical’ mechanism [19]. The ‘electromagnetic’ mechanism is due to the enhanced electromagnetic fields at or near nanometer size metallic particles. The ‘chemical’ mechanism is based on a charge transfer between the metallic surface and the nanotubes, which strongly depends on the electronic structure of the nanotubes. Our Raman results imply that there is charge transfer between gold nanoparticles and *s*-MWNTs, most probably, through the interlinker of PHT.

In conclusion, gold nanoparticles were self-assembled onto the surface of solubilized carbon nanotubes through a bi-functionalized molecule PHT. While the fluorescence of PHT is almost totally quenched by the binding of gold nanoparticles, the enhancement of the Raman responses of nanotubes is observed. Our results imply there are charge transfer interactions between nanotubes and gold nanoparticles, most probably through the interlinker of PHT.

Acknowledgements

We thank the Chinese Academy of Sciences and the Major State Basic Research Development Program (Grant No. G2000077500) for financial support.

References

- [1] A. Hirsh, *Angew. Chem. Int. Ed.* 41 (2002) 1853.
- [2] J.L. Bahr, J.M. Tour, *J. Mater. Chem.* 12 (2002) 1952.
- [3] J. Chen, M.A. Hamon, H. Hu, Y. Chen, A.M. Rao, P.C. Eklund, R.C. Haddon, *Science* 282 (1998) 95.
- [4] R.J. Chen, Y. Zhang, D. Wang, H. Dai, *J. Am. Chem. Soc.* 123 (2001) 3838.
- [5] J. Liu, A.G. Rinzler, H. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, T. Iverson, K. Shelimov, C.B. Huffman, F. Rodriguez-Macias, Y. Shon, T.R. Lee, D.T. Colbert, R.E. Smalley, *Science* 280 (1998) 1253.
- [6] H. Ago, K. Petrisch, M.S.P. Shaffer, A.H. Windle, R.H. Friend, *Adv. Mater.* 11 (1999) 1281.
- [7] A. Star, D.W. Steuerman, J.R. Heath, J.F. Stoddart, *Angew. Chem. Int. Ed.* 41 (2002) 2508.
- [8] S. Fullam, D. Cottell, H. Rensmo, D. Fitzmaurice, *Adv. Mater.* 12 (2000) 1430.
- [9] P.W. Chiu, G.S. Duesberg, U. Dettlaff-Weglikowska, S. Roth, *Appl. Phys. Lett.* 80 (2002) 3811.
- [10] L. Liu, S. Zhang, T. Hu, Z.-X. Guo, C. Ye, L. Dai, D. Zhu, *Chem. Phys. Lett.* 259 (2002) 191.

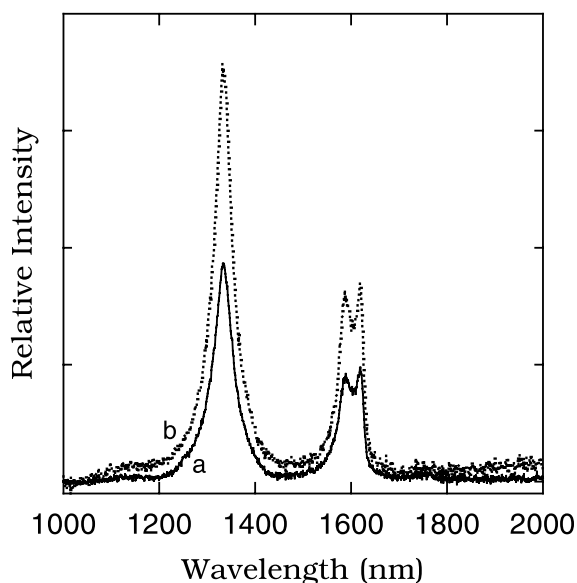


Fig. 5. Raman spectra of *s*-MWNTs (trace a) and *s*-MWNTs bound with gold nanoparticles through PHT (trace b).

- [11] T. Wang, D. Zhang, W. Xu, J. Yang, R. Han, D. Zhu, *Langmuir* 18 (2002) 1840.
- [12] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, *Chem. Commun.* (1994) 801.
- [13] A. Star, J.F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E.W. Wong, X. Yang, S.-W. Chung, H. Choi, J.R. Heath, *Angew. Chem. Int. Ed.* 40 (2001) 1721.
- [14] J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, London, 1970.
- [15] Y.-P. Sun, J.E. Riggs, Z.-X. Guo, H.W. Rollins, in: J. Shinar, Z.V. Vardeny, Z.H. Kafafi (Eds.), *Optical and Electronic Properties of Fullerenes and Fullerene-Based Materials*, Marcel-Dekker, New York, 2000, p. 43.
- [16] P.K. Sudeep, B.I. Ipe, K.G. Thomas, M.V. George, S. Barazzouk, S. Hotchandani, P.V. Kamat, *Nano Lett.* 2 (2002) 29.
- [17] L. Liu, Z.X. Guo, D. Zhu, *Carbon*, 2002, in press.
- [18] P. Tan, S.L. Zhang, K.T. Yue, F. Huang, Z. Shi, X. Zhou, Z. Gu, *J. Raman Spectrosc.* 28 (1997) 369.
- [19] P. Corio, S.D.M. Brown, A. Marucci, M.A. Pimenta, K. Kneipp, G. Dresselhaus, M.S. Dresselhaus, *Phys. Rev. B* 61 (2001) 13202.
- [20] K. Kneipp, H. Kneipp, P. Corio, S.D.M. Brown, K. Shafer, J. Motz, L.T. Perelman, E.B. Hanlon, A. Marucci, G. Dresselhaus, M.S. Dresselhaus, *Phys. Rev. Lett.* 84 (2000) 3470.
- [21] K. Kneipp, A. Jorio, H. Kneipp, S.D.M. Brown, K. Shafer, J. Motz, R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Phys. Rev. B* 63 (2001) 081401.
- [22] H. Grebel, Z. Iqbal, A. Lan, *Chem. Phys. Lett.* 348 (2001) 203.
- [23] S. Lefrant, I. Baltog, M. Baibarac, J. Schreiber, O. Chauver, *Phys. Rev. B* 65 (2002) 235401.