COMMUNICATION www.rsc.org/chemcomm | ChemComm

Modification of multi-wall carbon nanotube surfaces with poly(amidoamine) dendrons: Synthesis and metal templating†

Lei Tao,[a] Gaojian Chen,[a] Giuseppe Mantovani,[a] Steve York[b] and David M. Haddleton*[a]

Received (in Cambridge, UK) 27th June 2006, Accepted 14th September 2006
First published as an Advance Article on the web 9th October 2006
DOI: 10.1039/b609065f

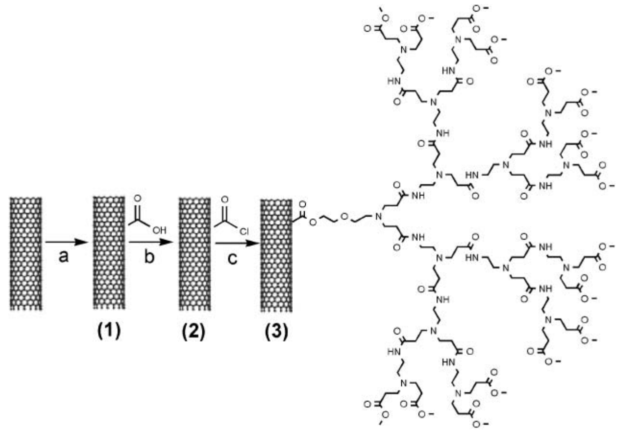
Hydroxyl functional poly(amidoamine) dendron wedges have been reacted with the surface of multi-walled carbon nanotubes and used for templating silver nanoparticles.

Carbon nanotubes (CNT's) have attracted considerable interest since their discovery in 1991.[1] They exhibit appealing electronic features as well as remarkable thermal and mechanical properties. For example, CNT's have been reacted with nanoparticles[2–5] and protein/genes[6–8] which have resulted in their use in diverse applications including chemical sensors, catalysts and protein/gene transporters. However, in some cases their practical use has been hampered by poor solubility, in both organic solvents and water. Modification of CNT's with polymers is a commonly used strategy to overcome this problem. Both branched[9,10] and linear synthetic polymers[11–20] have been used for this purpose. The resulting hybrid conjugates show superior solubility over unmodified CNT's in addition to a number of interesting chemical and physical properties, intrinsic to the conjugate used in the modification.

Star-shaped CNT's have been previously prepared using poly(amidoamine) dendrimer (PAMAM) with amine as peripheral groups as a cross-linking reagent.[21] PAMAM dendrimers have been utilized in different fields since their discovery in 1985.[22,23] Their ability of interacting with anionic materials such as DNA has led to their use in pharmaceuticals as potential gene delivery therapeutics[13,24–27] and templates for dendrimer-coated metal nanoparticles.[28–40] PAMAM dendrimers have also been employed as protein/enzyme mimics due to their structural similarities to natural proteins and to coat solid surfaces.[41–43]

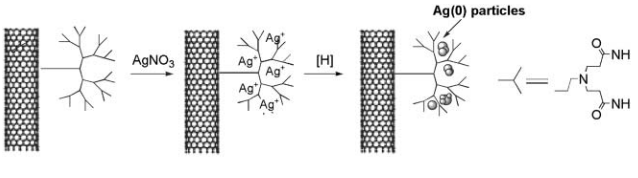
Herein, we describe the functionalisation of the surface of CNT's with PAMAM derivatives which, to the best of our knowledge, is the first chemical modification of CNT's with dendrimers.[44] 2-(2-Amino-ethoxy)-ethanol, was used to prepare the required hydroxyl-terminated PAMAM dendron (**4**). Four dendrimer generations were grown by sequential double Michael additions of methylacrylate to primary amines followed by amidation with a large excess of ethylene diamine (see supporting information†).

Commercially available multi-wall CNT's (MWCNT's) were treated with nitric acid to form carboxyl groups at the surface (**1**) followed by reaction with thionyl chloride to give the corresponding acid chlorides (**2**) (Scheme 1) prior to conjugation with focal point monohydroxyl-functionalised dendrons *via* ester linkages to give the expected PAMAM–MWCNT's hybrid material. Direct detection of the dendrons grafted at the MWCNT's surface using TEM microscopy proved to be problematic due to the relatively small size of the dendron. We reasoned that the deposition of appropriate metal particles onto the CNT's surface using dendrimers as templates could furnish a direct observable proof of the presence of dendrimers at the surface of the nanotubes, whilst also highlighting the potential application of these hybrid materials to act as starting materials for the preparation of more complex nanomaterials. Addition of formaldehyde as a reducing agent to a hydroxyl-terminated PAMAM dendron (**4**)–$AgNO_3$ solution led to the precipitation of Ag(0) particles in less than three seconds. The test was then repeated using the PMAM–MWCNT's conjugate (**3**) in place of the unmodified dendron (**4**) (Scheme 2).



Scheme 1 Reagents and conditions: (a) nitric acid, (b) thionyl chloride.

Thermal gravimetric analysis (TGA, Fig. 1) of the MWCNT's starting material (curve 1) and MWCNT's–COOH (**1**) (curve 2) gave very similar results, with no significant weight loss up to *ca.* 400 °C. At the same temperature the PAMAM–MWCNT conjugate (**3**) (curve 3) showed 39% weight loss ascribed to the presence of the dendron grafted onto the surface (Fig. 1). As expected the Ag(0)-containing material (curve 4) showed a profile analogous to that of the unmodified conjugate (**3**), with lower



Scheme 2 Synthesis of dendrimer–MWCNT–Ag(0) hybrid materials.

---

[a] *Department of Chemistry, University of Warwick, Coventry, UK. E-mail: D.M.Haddleton@warwick.ac.uk; Tel: +44 024 7652 3256*
[b] *Department of Physics, University of Warwick, Coventry, UK*

† Electronic supplementary information (ESI) available: Synthesis and characterization of HO-PAMAM dendrimer (**4**) and the corresponding CNTs conjugate (**3**). See DOI: 10.1039/b609065f

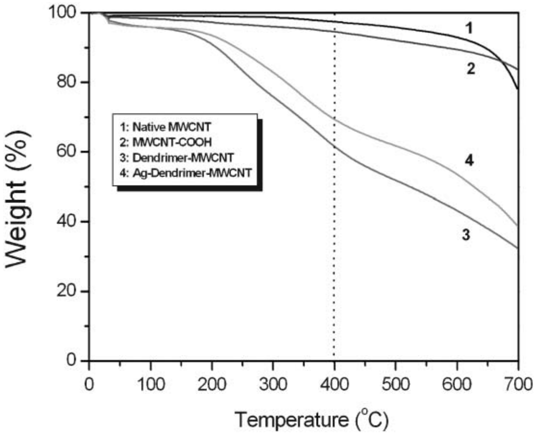


Fig. 1 TGA of native and functionalized MWCNT's.

percentage weight loss. This is consistent with the lower dendron content of this material, due to the presence of an estimate 23% weight content of Ag(0).

Transmission electron microscopy (TEM) images of the MWCNT's before and after modification with the hydroxyl-PAMAM (**4**) are shown in Fig. 2.

Energy-dispersive spectral (EDS) analysis of the micrographs showed that Ag(0) could only be detected at the surface of MWCNT–dendron conjugate (3.0 K ev) (Fig. 2D and E). This indicates nanoparticle formation occurs *via* Ag(I) coordination to the PAMAM dendron nitrogen donors, followed by reduction with formaldehyde. No silver deposition was observed neither in the background (Fig. 2D) nor with MWCNT-COOH (**1**) (Fig. 2C), in agreement with the proposed mechanism.

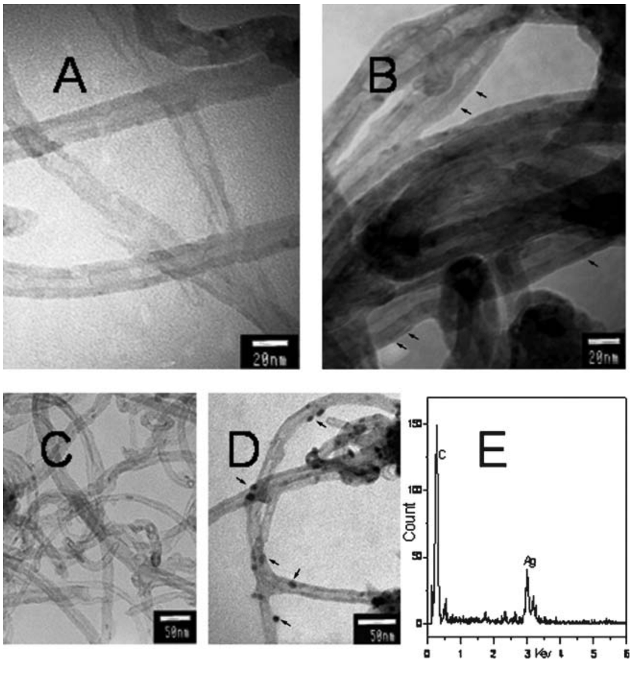


Fig. 2 TEM images of: (A) MWCNT's; (B) dendron–MWCNT conjugate (**3**); (C) MWCNT-COOH (**1**) + $AgNO_3$ + formaldehyde; (D) dendrimer–MWCNT (**3**) + $AgNO_3$ + formaldehyde; (E) EDS spectrum of Ag–dendrimer–MWCNT's.

In summary, novel hydroxy-terminated dendrons have been prepared and covalently linked to MWCNT's *via* ester bonds. The corresponding dendron–MWCNT's conjugates have been characterized by FT-IR, TGA, and TEM. In addition these hybrid materials have been employed as templates for the deposition of Ag(0) nanoparticles, *via* dendrimer coordination of Ag(I) ions, followed by reduction with formaldehyde. Silver particles were visible on the nanotubes surface by TEM/EDS analysis.

The ability of these dendron–carbon nanotubes to undergo gene absorption and their potential in a number of other potential applications are currently under investigation.

Notes and references

1 S. Iijima, *Nature*, 1991, **354**, 56–58.
2 A. Bezryadin, C. N. Lau and M. Tinkham, *Nature*, 2000, **404**, 971–974.
3 T. M. Day, P. R. Unwin, N. R. Wilson and J. V. Macpherson, *J. Am. Chem. Soc.*, 2005, **127**, 10639–10647.
4 J. Kong, M. G. Chapline and H. Dai, *Adv. Mater.*, 2001, **13**, 1384–1386.
5 J. H. Lee, Y.-b. Lim, J. S. Choi, Y. Lee, T.-i. Kim, H. J. Kim, J. K. Yoon, K. Kim and J.-s. Park, *Bioconjugate Chem.*, 2003, **14**, 1214–1221.
6 R. J. Chen, Y. Zhang, D. Wang and H. Dai, *J. Am. Chem. Soc.*, 2001, **123**, 3838–3839.
7 N. W. S. Kam and H. Dai, *J. Am. Chem. Soc.*, 2005, **127**, 6021–6026.
8 K. Wada, H. Arima, T. Tsutsumi, Y. Chihara, K. Hattori, F. Hirayama and K. Uekama, *J. Controlled Release*, 2005, **104**, 397–413.
9 L. Cao, W. Yang, J. Yang, C. Wang and S. Fu, *Chem. Lett.*, 2004, **33**, 490–491.
10 C.-Y. Hong, Y.-Z. You, D. Wu, Y. Liu and C.-Y. Pan, *Macromolecules*, 2005, **38**, 2606–2611.
11 J. E. Riggs, Z. Guo, D. L. Carroll and Y.-P. Sun, *J. Am. Chem. Soc.*, 2000, **122**, 5879–5880.
12 D. E. Hill, Y. Lin, A. M. Rao, L. F. Allard and Y.-P. Sun, *Macromolecules*, 2002, **35**, 9466–9471.
13 X.-Q. Zhang, X.-L. Wang, S.-W. Huang, R.-X. Zhuo, Z.-L. Liu, H.-Q. Mao and K. W. Leong, *Biomacromolecules*, 2005, **6**, 341–350.
14 S. Qin, D. Qin, W. T. Ford, D. E. Resasco and J. E. Herrera, *Macromolecules*, 2004, **37**, 752–757.
15 S. Qin, D. Qin, W. T. Ford, J. E. Herrera, D. E. Resasco, S. M. Bachilo and R. B. Weisman, *Macromolecules*, 2004, **37**, 3965–3967.
16 C. Gao, C. D. Vo, Y. Z. Jin, W. Li and S. P. Armes, *Macromolecules*, 2005, **38**, 8634–8648.
17 R. Czerw, Z. Guo, P. M. Ajayan, Y.-P. Sun and D. L. Carroll, *Nano Lett.*, 2001, **1**, 423–427.
18 Z. Yao, N. Braidy, G. A. Botton and A. Adronov, *J. Am. Chem. Soc.*, 2003, **125**, 16015–16024.
19 D. Baskaran, J. W. Mays and M. S. Bratcher, *Angew. Chem.*, 2004, **43**, 2138–2142.
20 Y. Lin, B. Zhou, K. A. S. Fernando, P. Liu, L. F. Allard and Y.-P. Sun, *Macromolecules*, 2003, **36**, 7199–7204.
21 M. Sano, A. Kamino and S. Shinkai, *Angew. Chem.*, 2001, **40**, 4661–4663.
22 D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Polym. J.*, 1985, **17**, 117–132.
23 D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Macromolecules*, 1986, **19**, 2466–2468.
24 A. Bielinska, J. F. Kukowska-Latallo, J. Johnson, D. A. Tomalia and J. R. Baker, Jr., *Nucleic Acids Res.*, 1996, **24**, 2176–2182.
25 C. S. Braun, J. A. Vetro, D. A. Tomalia, G. S. Koe, J. G. Koe and C. R. Middaugh, *J. Pharm. Sci.*, 2005, **94**, 423–436.
26 T.-I. Kim, H. J. Seo, J. S. Choi, H.-S. Jang, J. Baek, K. Kim and J.-S. Park, *Biomacromolecules*, 2004, **5**, 2487–2492.
27 N. Malik, R. Wiwattanapatapee, R. Klopsch, K. Lorenz, H. Frey, J. W. Weener, E. W. Meijer, W. Paulus and R. Duncan, *J. Controlled Release*, 2000, **65**, 133–148.
28 C. J. Hawker and K. L. Wooley, *Science*, 2005, **309**, 1200–1204.
29 B. L. Frankamp, A. K. Boal and V. M. Rotello, *J. Am. Chem. Soc.*, 2002, **124**, 15146–15147.
30 J. C. Garcia-Martinez and R. M. Crooks, *J. Am. Chem. Soc.*, 2004, **126**, 16170–16178.

This journal is © The Royal Society of Chemistry 2006

31 J. C. Garcia-Martinez, R. Lezutekong and R. M. Crooks, *J. Am. Chem. Soc.*, 2005, **127**, 5097–5103.

32 J. C. Garcia-Martinez, R. W. J. Scott and R. M. Crooks, *J. Am. Chem. Soc.*, 2003, **125**, 11190–11191.

33 R. W. J. Scott, H. Ye, R. R. Henriquez and R. M. Crooks, *Chem. Mater.*, 2003, **15**, 3873–3878.

34 Y. Gu, H. Xie, J. Gao, D. Liu, C. T. Williams, C. J. Murphy and H. J. Ploehn, *Langmuir*, 2005, **21**, 3122–3131.

35 H. Lang, R. A. May, B. L. Iversen and B. D. Chandler, *J. Am. Chem. Soc.*, 2003, **125**, 14832–14836.

36 A. Singh and B. D. Chandler, *Langmuir*, 2005, **21**, 10776–10782.

37 R. W. J. Scott, A. K. Datye and R. M. Crooks, *J. Am. Chem. Soc.*, 2003, **125**, 3708–3709.

38 R. W. J. Scott, C. Sivadinarayana, O. M. Wilson, Z. Yan, D. W. Goodman and R. M. Crooks, *J. Am. Chem. Soc.*, 2005, **127**, 1380–1381.

39 R. W. J. Scott, O. M. Wilson, S.-K. Oh, E. A. Kenik and R. M. Crooks, *J. Am. Chem. Soc.*, 2004, **126**, 15583–15591.

40 B. L. Frankamp, A. K. Boal, M. T. Tuominen and V. M. Rotello, *J. Am. Chem. Soc.*, 2005, **127**, 9731–9735.

41 G. J. Bahun, C. Wang and A. Adronov, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 1941–1951.

42 A. Dahan and M. Portnoy, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 235–262.

43 S. Reemers, A. Mourran, H. Keul and M. Möller, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 1372–1386.

44 While this manuscript was in preparation, an independent account of synthesis of different dendrimer–CNT's materials was reported: S.-H. Hwang, C. N. Moorefield, P. Wang, K.-U. Jeong, S. Z. D. Cheng, K. K. Kotta and G. R. Newkome, *J. Am. Chem. Soc.*, 2006, **128**, 7505–7509.

Find a SOLUTION

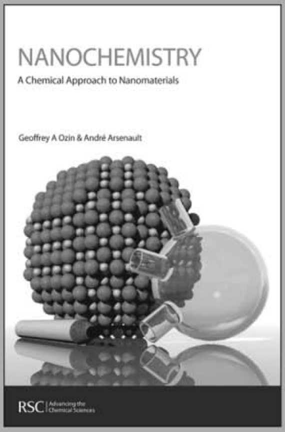
… with books from the RSC

Choose from exciting textbooks, research level books or reference books in a wide range of subject areas, including:

- Biological science
- Food and nutrition
- Materials and nanoscience
- Analytical and environmental sciences
- Organic, inorganic and physical chemistry

Look out for 3 new series coming soon …

- RSC Nanoscience & Nanotechnology Series
- Issues in Toxicology
- RSC Biomolecular Sciences Series



28040542

RSC | Advancing the Chemical Sciences

www.rsc.org/books