Carbon-Nanotube-Templated and Pseudorotaxane-Formation-Driven Gold Nanowire Self-Assembly

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A cation-modified multiwalled carbon nanotube is used to template the noncovalent self-assembly in solution of a gold nanowire from crown-modified gold nanoparticles. The driving force for self-assembly is formation of the surface-confined pseudorotaxane that results from the electron-poor cation threading the electron-rich crown.

Introduction

The demand for integrated circuits that will allow information to be processed at even faster speeds remains undiminished. This is despite the fact that the density of the wires and switches that comprise such circuits has doubled every eighteen months for nearly four decades, giving rise to Moore's Law.[1]

It is clear that Moore's Law will hold true until 2012; it is not clear that it will hold true thereafter.[2] The responses of the relevant technological and scientific communities have been two-fold: first, to continue to develop existing fabrication and materials technologies; and second, to consider alternative fabrication and materials technologies.

When considering alternative fabrication technologies, one is attracted to the self-assembly in solution and self-organization at a conventionally patterned silicon wafer substrate of nanoscale wires and switches.[3] When considering alternative materials technologies, one is attracted to the use of the growing number of nanoscale condensed-phase and molecular building blocks that are becoming available.[4]

Specifically, one is attracted to the use of nanoscale condensed-phase and molecular building blocks to self-assemble in solution and self-organize at a patterned silicon wafer substrate metal nanowires.[5]

It was in this context that Fullam et al. previously reported the multiwalled carbon nanotube (MWNT) templated self-assembly of gold nanowires from gold nanoparticles.[6] Briefly, unmodified MWNTs added to a stable dispersion of tetraoctylammonium bromide (TOAB)-modified gold nanoparticles templated the assembly in solution of gold nanowires comprised of discrete gold nanoparticles. It was suggested that the driving force for self-assembly was charge transfer from the conduction band states of the gold nanoparticle to the π^* states of the carbon nanotubes.[7]

It is noted that there has been a large number of subsequent reports describing the preparation of metal- and metal-oxide-coated carbon nanotubes.[8] It is also noted that there has been a large number of reports describing the chemical modification of carbon nanotubes. Initially, these reports focused on the covalent introduction of carboxy groups at the surface of the carbon nanotubes.[9] Subsequently, these reports have focused on the covalent coupling of an increasingly wide range of functional molecules and biomolecules to the surface of carboxy-modified carbon nanotubes.[10]

Reported herein is the preparation of cation-modified (dibenzylammonium) MWNTs and crown-modified (dibenzo[24]crown-8) gold nanoparticles (Scheme 1). It was expected that the above cation-modified MWNTs would

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(1) Moore, G. *Electronics* **1965**, *38*, 114.

(2) International Technology Roadmap for Semiconductors, **2002** (http://public.itrs.net/).

(3) Parviz, B.; Ryan, D.; Whitesides, G. *IEEE Trans. Adv. Pac.* **2003**, *26*, 233.

(4) Parak, W.; Gerion, D.; Pellegrino, T.; Zanchet, D.; Micheel, C.; Williams, S.; Boudreau, R.; Le Gros, M.; Larabell, C.; Alivisatos, A. *Nanotechnology* **2003**, *14*, 15.

(5) Richter, J. *Physica E* **2003**, *16*, 157.

(6) Fullam, S.; Rensmo, H.; Cottell, D.; Fitzmaurice, D. *Adv. Mater.* **2000**, *12*, 1430.

(7) (a) Brust, M.; Kiely, C.; Bethell, D.; Schiffrin, D. *J. Am. Chem. Soc.* **1998**, *120*, 12367. (b) Maxwell, A.; Bruhwiler, P.; Nilsson, A.; Martensson, N. *Phys. Rev. B* **1994**, *49*, 10717. (c) Hunt, M.; Modesti, S.; Rudolf, P.; Palmer, R. *Phys. Rev. B* **1995**, *51*, 10039.

(8) (a) Satishkumar, B.; Vogl, E.; Govindaraj, A.; Rao, C. *J. Phys. D: Appl. Phys.* **1996**, *29*, 3173. (b) Zhang, Y.; Franklin, N.; Chen, R.; Dai, H. *Chem. Phys. Lett.* **2000**, *331*, 35. (c) Banerjee, S.; Wong, S. *Nano Lett.* **2002**, *2*, 195. (d) Li, Y.; Ding, J.; Chen, J.; Cailu, X.; Wei, B.; Liang, J.; Wu, D. *Mater. Res. Bull.* **2002**, *1847*, 1. (e) Azamian, B.; Coleman, K.; Davis, J.; Hanson, N.; Green, M. *Chem. Commun.* **2002**, 366. (f) Fu, Q.; Lu, C.; Liu, J. *Nano Lett.* **2002**, *2*, 329. (g) Choi, H.; Shim, M.; Bangsaruntip, S.; Dai, H. *J. Am. Chem. Soc.* **2002**, *124*, 9058. (h) Haremza, J.; Hahn, M.; Krauss, T.; Chen, S.; Calcines, J. *Nano Lett.* **2002**, *2*, 1253. (i) Han, W.-Q.; Zettl, A. *J. Am. Chem. Soc.* **2003**, *125*, 2062. (j) Ellis, A.; Vijayamohanan, K.; Goswami, R.; Chakrapani, N.; Ramanathan, L.; Ajayan, P.; Ramanath, G. *Nano Lett.* **2003**, *3*, 279. (k) Jiang, K.; Eitan, A.; Schadler, L.; Ajayan, P.; Siegel, R.; Grobert, N.; Mayne, M.; Reyes-Reyes, M.; Terrones, H.; Terrones, M. *Nano Lett.* **2003**, *3*, 275. (l) Ravindran, S.; Chaudhary, S.; Colburn, B.; Ozkan, M.; Ozkan, C. *Nano Lett.* **2003**, *3*, 447. (m) Han, W.-Q.; Zettl, A. *Nano Lett.* **2003**, *3*, 681.

(9) (a) Hiura, H. *Mol. Cryst. Liq. Cryst.* **1995**, *267*, 267. (b) Hiura, H.; Ebbesen, T.; Tanigaki, K. *Adv. Mater.* **1995**, *7*, 275. (c) Ebbesen, T.; Hiura, H.; Bisher, M.; Tracey, M.; Shreeve-Keyer, J.; Haushalter, R. *Adv. Mater.* **1996**, *8*, 155. (d) Dujardin, E.; Ebbesen, T.; Krishnan, A.; Treacy, M. *Adv. Mater.* **1998**, *10*, 611. (e) Burghard, M.; Krstic, V.; Duesberg, G.; Philipp, G.; Muster, J.; Roth, S. *Synth. Met.* **1999**, *103*, 2540. (f) Satishkumar, B.; Govindaraj, A.; Mofokeng, J.; Subbanna, G.; Rao, C. *J. Phys. B: At. Mol. Opt.* **1996**, *29*, 4925. (g) Dillon, A.; Gennett, T.; Jones, K.; Alleman, J.; Parilla, P.; Heben, M. *Adv. Mater.* **1999**, *11*, 1354.

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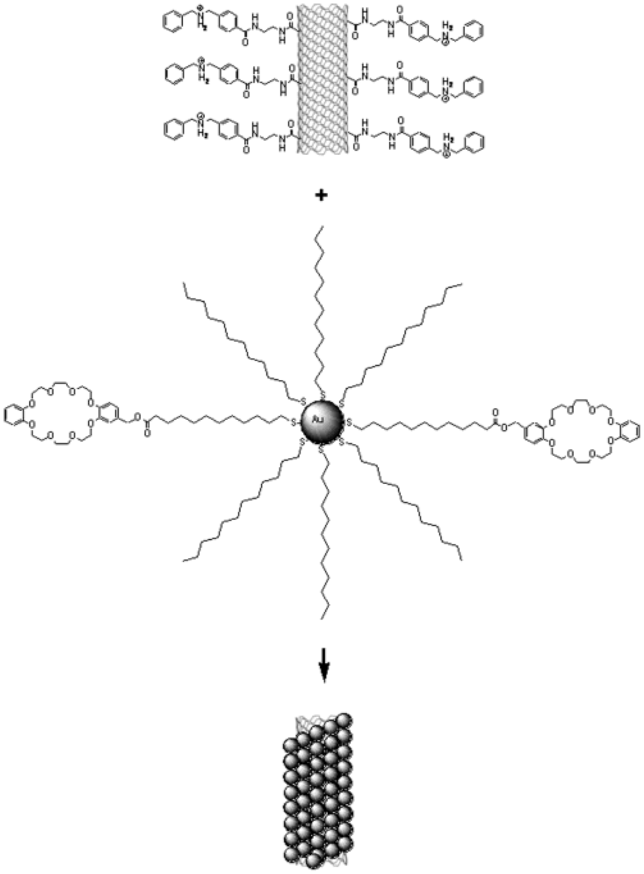
Scheme 1. A Cation-Modified Multiwalled Carbon Nanotube Templates the Noncovalent Self-Assembly in Solution of a Gold Nanowire from Crown-Modified Gold Nanoparticles



template the noncovalent self-assembly in solution of a gold nanowire from the above crown-modified gold nanoparticles (also Scheme 1).

This expectation was based on the fact that the electron-poor cation threads the electron-rich crown in solution to form a pseudorotaxane.[11] This expectation was also based on the fact that cation-modified silica and crown-modified silver nanoparticles self-assemble in solution, and that self-assembly is driven by formation of the corresponding surface-confined pseudorotaxane.[12]

Experimental Methods

All solvents and compounds were used as supplied by the Sigma-Aldrich Chemical Co. Ltd., unless otherwise stated.

Visible absorption spectra were recorded using a HP-8452A spectrophotometer with LabView software written to acquire the data. All visible absorption spectra were recorded against appropriate solvent or solution backgrounds.

All TEMs were obtained using a JEOL 2000 FX TEMscan (at an accelerating voltage of 80 kV) for samples deposited on both uncoated (2000 mesh) and carbon-coated (400 mesh) copper grids. The preparation of samples for TEM analysis involved the deposition of a drop of the relevant sample onto the above grids. The excess sample was removed by wicking and the grid was allowed to dry in air.

Preparation of Unmodified and Crown-Modified Gold Nanoparticles. A stable dispersion of dodecanethiol-modified gold nanoparticles was prepared in chloroform using a method similar to that described by Brust et al.[13] These nanoparticles were size-selectively precipitated to isolate a relatively size-monodisperse fraction (7.7 nm diameter, polydispersity 1.13). The near size-monodisperse fraction was subsequently modified by exchange of the adsorbed thiol for a thiol incorporating a crown. The above exchange was promoted using a method similar to that described by Ahern et al.[14]

Purification of Unmodified MWNTs. As-received MWNTs (MER Corporation, 3×10^{-3} g) were suspended by sonication (15 min) in chloroform (20 mL). The resulting suspension was centrifuged (5000 rpm, 15 min) and the supernatant fraction (approximately 75 vol %) was retained. This procedure was repeated a further three times, with the supernatant fraction being retained in each case.

Preparation of Carboxy-Modified MWNTs. MWNTs were treated as described following the method reported by Burghard et al. to introduce carboxy groups at the surface of the nanotubes.[15] This was achieved by refluxing the as-received MWNTs in nitric acid to produce hydroxyl, carbonyl, and carboxy groups at defects in the nanotube carbon lattice. The above hydroxyl and carbonyl groups were further oxidized to carboxy groups by treatment of the oxidized MWNTs with potassium permanganate and perchloric acid as described below.

Specifically, MWNTs (3.2×10^{-3} g) were added to nitric acid (3 mL, 69 wt %) and sonicated to ensure they were dispersed. The resulting suspension of MWNTs was refluxed under magnetic stirring (4 h, 130 °C) to oxidize the suspended MWNTs. The oxidized suspension of MWNTs was cooled and filtered using a polycarbonate membrane (Whatman-UK, 0.2-μm pore diameter) and washed with deionized water (200 mL). The oxidized MWNTs retained on the membrane were dispersed in deionized water (10 mL) by sonication. An acidic solution of potassium permanganate (9×10^{-3} g, 5.7×10^{-5} mol) and perchloric acid (3 mL, 50 wt %) was then added to the stirring solution. The potassium permanganate was quenched after 10 min by the addition of a solution of citric acid (0.133 g, 6.3×10^{-4} mol). The suspension was filtered using a polycarbonate membrane (Whatman-UK, 0.2-μm pore diameter) and washed with deionized water (200 mL). The resulting carboxy-modified MWNTs (3.0×10^{-3} g) were dispersed in deionized water (10 mL) by sonication.

TEMs of the MWNTs were obtained before and after the above oxidative process. A drop of one of the following suspensions was deposited onto a carbon-coated copper grid: unmodified MWNTs (3×10^{-3} g) in chloroform (10 mL), or carboxy-modified MWNTs (3×10^{-3} g) in water (10 mL).

Preparation of Cation-Modified MWNTs. The required cation-precursor, *N*-(4-carboxydibenzylamine)carbamate 6-

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(10) (a) Huang, W.; Lin, Y.; Taylor, S.; Gaillard, J.; Rao, A.; Sun, Y.-P. *Nano Lett.* **2002**, *2*, 231. (b) Huang, W.; Taylor, S.; Fu, K.; Lin, Y.; Zhang, D.; Hanks, T.; Rao, A.; Sun, Y.-P. *Nano Lett.* **2002**, *2*, 311. (c) Pompeo, F.; Resasco, D. *Nano Lett.* **2002**, *2*, 369. (d) Shim, M.; Wong Shi Kam, N.; Chen, R.; Li, Y.; Dai, H. *Nano Lett.* **2002**, *2*, 285. (e) Kahn, M.; Banerjee, S.; Wong, S. *Nano Lett.* **2002**, *2*, 1215. (f) Frehill, F.; Vos, J.; Benrezzak, S.; Koos, A.; Konya, Z.; Ruther, M.; Blau, W.; Fonseca, A.; Nagy, J.; Biro, L.; Minett, A.; in het Panhuis, M. *J. Am. Chem. Soc.* **2002**, *124*, 13694. (g) Star, A.; Liu, Y.; Grant, K.; Ridvan, L.; Stoddart, F.; Steuerman, D.; Diehl, M.; Boukai, A.; Heath, J. *Macromol.* **2003**, *36*, 553. (h) Stevens, J.; Huang, A.; Peng, H.; Chiang, I.; Khabashesku, V.; Margrave, J. *Nano Lett.* **2003**, *3*, 331. (i) Chambers, G.; Carroll, C.; Farrell, G.; Dalton, A.; McNamara, M.; in het Panhuis, M.; Byrne, H. *Nano Lett.* **2003**, *3*, 843. (j) Besteman, K.; Lee, J.-O.; Wiertz, F.; Heering, H.; Dekker, C. *Nano Lett.* **2003**, *3*, 727.

(11) (a) Ashton, P.; Campbell, P.; Chrystal, E.; Glink, P.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J.; Tasker, P.; Williams, D. *Angew. Chem. Intl. Ed. Engl.* **1995**, *17*, 1865. (b) Ashton, P.; Fyfe, M.; Hickingbottom, S.; Menzer, S.; Stoddart, J.; White, A.; Williams, D. *Chem. Eur. J.* **1998**, *4*, 577.

(12) (a) Fitzmaurice, D.; Rao, S.; Preece, J.; Stoddart, J.; Wenger, S.; Zaccheroni, N. *Angew. Chem. Intl. Ed.* **1999**, *38*, 1147. (b) Ryan, D.; Rao, S.; Rensmo, H.; Fitzmaurice, D.; Preece, J.; Wenger, S.; Stoddart, J.; Zaccheroni, N. *J. Am. Chem. Soc.* **2000**, *122*, 6252.

(13) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D.; Whyman, R. *J. Chem. Soc. Chem. Commun.* **1994**, 801.

(14) Ahern, D.; Rao, S.; Fitzmaurice, D. *J. Phys. Chem. B.* **1999**, *103*, 1821.

(15) Burghard, M.; Krstic, V.; Duesberg, G.; Philipp, G.; Muster, J.; Roth, S. *Synth. Met.* **1999**, *103*, 2540.

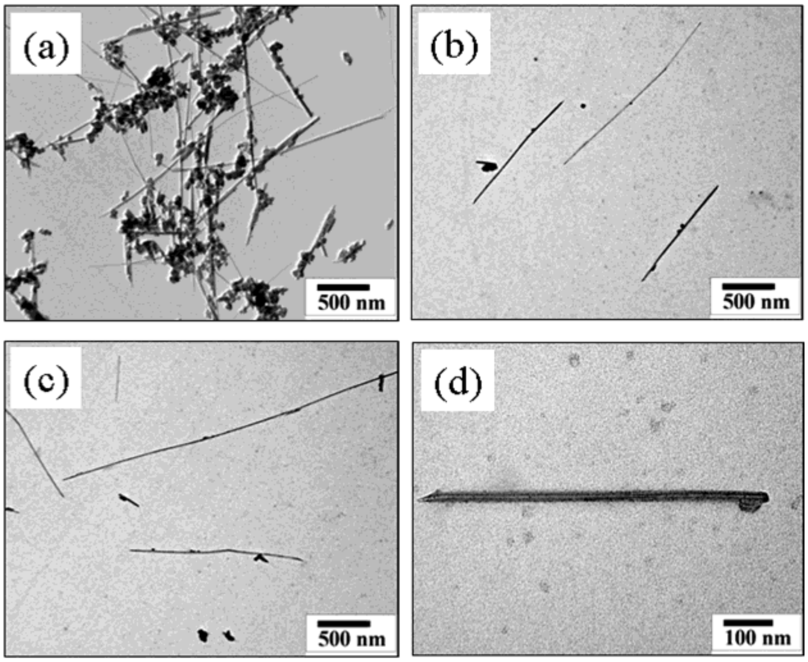


Figure 1. As-received multiwalled carbon nanotubes (a) prior to purification, (b) following purification, and (c and d) following carboxy-modification.

nitroveratryloxy chloroformate, was prepared as described in detail elsewhere.[16]

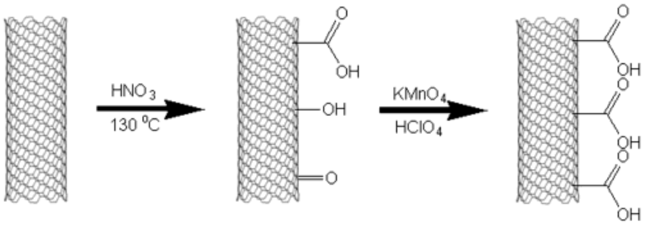
Modification of the MWNTs required two amide-coupling reactions: the first was between carboxy-modified MWNTs and ethylenediamine, and the second was between the remaining amine of the coupled ethylenediamine and the cation-precursor, as described below.

Specifically, ethylenediamine (5.6×10^{-6} mL, 8.3×10^{-4} mol) was added, followed by EDAC (1.91×10^{-1} g, 1×10^{-3} mol) and DMAP (12×10^{-3} g, 1×10^{-4} mol), to a suspension of carboxy-modified MWNTs (3×10^{-3} g) in water (10 mL), and the resulting suspension was stirred for 12 h. The suspension was filtered on a polycarbonate membrane (Whatman-UK, 0.2-μm pore diameter) and washed with deionized water (200 mL). The above membrane was sonicated in deionized water (10 mL) to recover the modified MWNTs. The water was removed using a rotary evaporator, which was followed by drying on a vacuum line (3 h).

The modified MWNTs were dispersed in anhydrous dichloromethane (10 mL) by sonication. The cation-precursor (10.6×10^{-3} g, 2.3×10^{-5} mol), followed 30 s later by EDAC (20×10^{-3} g, 1.0×10^{-4} mol) and DMAP (1.30×10^{-3} g, 1.0×10^{-5} mol), was added to the stirred suspension of the above modified MWNTs. The suspension was stirred for 16 h in a sealed flask in the absence of light. The material was filtered using an Anodisc filter membrane (Whatman-UK, 0.02-μm pore diameter), and washed with anhydrous dichloromethane (100 mL) followed by ethanol (100 mL). The above membrane was sonicated in ethanol (10 mL) to recover the cation-precursor-modified MWNTs.

The output from a UV-H 253 BL Ultra Violet 250-W UV lamp was used as the light source for photoactivation. Hexafluorophosphoric acid was added to a suspension of cation-precursor-modified-MWNTs (3×10^{-3} g) in ethanol (10 mL) until the pH was 2. The suspension was irradiated using the UV lamp for 2 h, filtered on a polycarbonate membrane (Whatman-UK, 0.2-μm pore diameter), and washed with ethanol (100 mL). This procedure results in the photoactivated deprotection of the dibenzylamine in acidic conditions in the presence of a counterion, PF_6^-. The resultant salt of the dibenzylammonium cation (cation) is formed. The cation-modified MWNTs were dispersed by sonication in ethanol (10 mL). The ethanol was removed by rotary evaporation followed by drying on a vacuum line (3 h). The dry cation-modified MWNTs were dispersed by sonication in chloroform (10 mL).

Scheme 2. Introduction of Carboxyl, Hydroxy, and Carbonyl Groups at the Defect Sites Present at the Surface of the As-Received Multiwalled Carbon Nanotubes Followed by Conversion of Carbonyl and Hydroxy Groups to Carboxy Groups



Templated Self-Assembly of Gold Nanowires. The templated self-assembly of gold nanowires from these components is described in detail in the Results and Discussion section of this paper and therefore is not described in this section.

Results and Discussion

Preparation and Characterization of Cation-Modified MWNTs. A TEM of the as-received MWNTs reveals that there is a significant amount of amorphous carbon present (Figure 1a). To remove this impurity, the above MWNTs were sonicated in chloroform, centrifuged, and filtered. A TEM of the purified MWNTs shows a well-dispersed sample with an average nanotube diameter of 24 nm and an average nanotube length of 2 μm (Figure 1b).

The oxidation of MWNTs under strongly acidic conditions results in the introduction of carboxylic, hydroxyl, and carbonyl groups at defect sites on the surface of the MWNTs in the approximate ratio 4:2:1 (Scheme 2).[9a-d] To maximize the number of functional groups suitable

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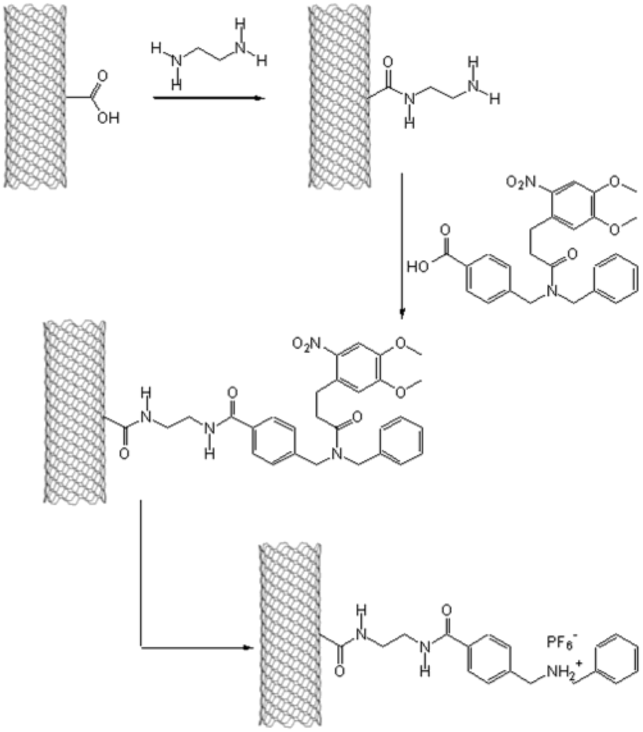
[16] (a) Ryan, D.; Nagle, L.; Rensmo, H.; Fitzmaurice, D. *J. Phys. Chem. B.* **2002**, *106*, 5371. (b) Ryan, D.; Nagle, L.; Fitzmaurice, D. *Nano Lett.*, published online Mar. 18, 2004, http://dx.doi.org/10.1021/nl0351340.

Scheme 3. Covalent Coupling of One End of the Ethylenediamine Linker to a Carbonyl Group Present at the Surface of a Carboxy-Modified Multiwalled Nanotube Followed by Coupling of the Other End of the Linker to the Cation Precursor



for covalent modification, the above hydroxy and carbonyl groups were subsequently oxidized to carboxy groups (Scheme 2).[9e] It is estimated that the density of carboxy groups present at the surface of the above carboxy-modified MWNT is 4.2 per 100 Å^2. This estimate is based on findings reported by Hiura and coworkers, concerning the number of carbon atoms at the surface of a known mass of MWNTs,[9a] and by Rao et al., concerning the number of carboxy groups present following acid oxidation of a known mass of MWNTs.[9f] A TEM of the carboxy-modified MWNTs shows a well-dispersed material with an average diameter of 24 nm and an average length of 2 μm (Figure 1c and d).

The cation-precursor (*N*-(4-carboxydibenzylamine)-carbamate-6-nitroveratryloxy chloroformate) was covalently coupled to the surface of the carboxy-modified MWNTs. Because the carboxy-modified MWNTs and cation precursor both have carboxy moieties, ethylenediamine was deemed a suitable linker. Coupling was achieved by EDAC-catalyzed amide formation between the carboxy-modified MWNTs and ethylenediamine, and between ethylenediamine and the carboxy group of the cation precursor (Scheme 3). To minimize the possibility of cross-linking of MWNTs, the amount of ethylenediamine used was in excess of the number of carboxy groups present at the surface of the MWNTs.

No aggregation of the MWNTs was observed before or after the above reaction. The surface density of attached molecules in the resulting cation-precursor-modified MWNTs was estimated to be 2.7 per 100 Å^2, assuming a yield of 80% for each amide formation step.

The cation-modified MWNT-templated self-assembly of crown-modified gold nanoparticles requires the prior deprotection of the cation precursor under acidic conditions to form the cation. This is achieved by photolysis of the cation precursor in the presence of hexafluorophosphoric acid.

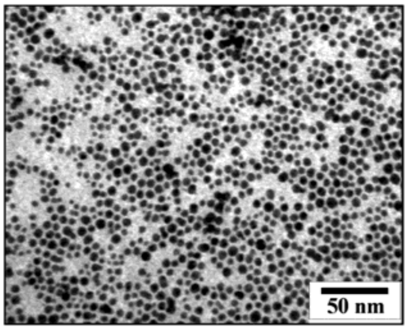


Figure 2. Crown-modified gold nanoparticles.

Preparation and Characterization of Modified Gold Nanoparticles. Briefly, thiol-modified (dodecanethiol) gold nanoparticles were prepared using a method similar to that reported by Brust et al.[13] These nanoparticles were selectively precipitated to isolate a relatively size-monodisperse fraction. These nanoparticles were further modified by exchange of the initially adsorbed thiol molecules for crown-thiol molecules (dodecane thiol incorporating a crown moiety in the terminal position).[14] A TEM analysis of 200 nanoparticles yields an average diameter of 7.7 nm and a polydispersity of 1.13 (Figure 2).

Visible absorption spectroscopy confirmed the existence of the characteristic absorbance maximum at 520 nm, which was assigned to the surface plasmon resonance of the gold nanoparticles.

Templated Self-Assembly of Gold Nanowires. To initiate the templated self-assembly of a gold nanowire in solution, a dispersion of crown-modified gold nanoparticles (0.2 mL, 4×10^{12} nanoparticles mL^{-1}) in chloroform was added to a freshly sonicated suspension of cation-modified MWNTs (0.5 mL, 15×10^{-5} g mL^{-1}) also in chloroform. Following equilibration of this suspension for 24 h a black precipitate was obtained. TEM analysis revealed the formation of gold nanowires (Figure 3a).

A series of related control experiments was performed under similar conditions. Specifically, a dispersion of crown-modified gold nanoparticles (0.2 mL, 4×10^{12} nanoparticles mL^{-1}) in chloroform was added to a freshly sonicated suspension of cation-precursor-modified MWNTs (0.5 mL, 15×10^{-5} g mL^{-1}) also in chloroform. Following equilibration of this suspension for 24 h no black precipitate was observed. TEM analysis revealed no gold nanowire formation (Figure 3b).

A dispersion of crown-modified gold nanoparticles (0.2 mL, 4×10^{12} nanoparticles mL^{-1}) in chloroform was added to a freshly sonicated suspension of unmodified MWNTs (0.66 mL, 11×10^{-5} g mL^{-1}) also in chloroform. Following equilibration of this suspension for 24 h no black precipitate was observed. TEM analysis revealed no gold nanowire formation (Figure 3c).

A dispersion of thiol-modified gold nanoparticles (0.2 mL, 4×10^{12} nanoparticles mL^{-1}) in chloroform was added to a freshly sonicated suspension of cation-modified MWNTs (0.5 mL, 5×10^{-5} g mL^{-1}) also in chloroform. Following equilibration of this suspension

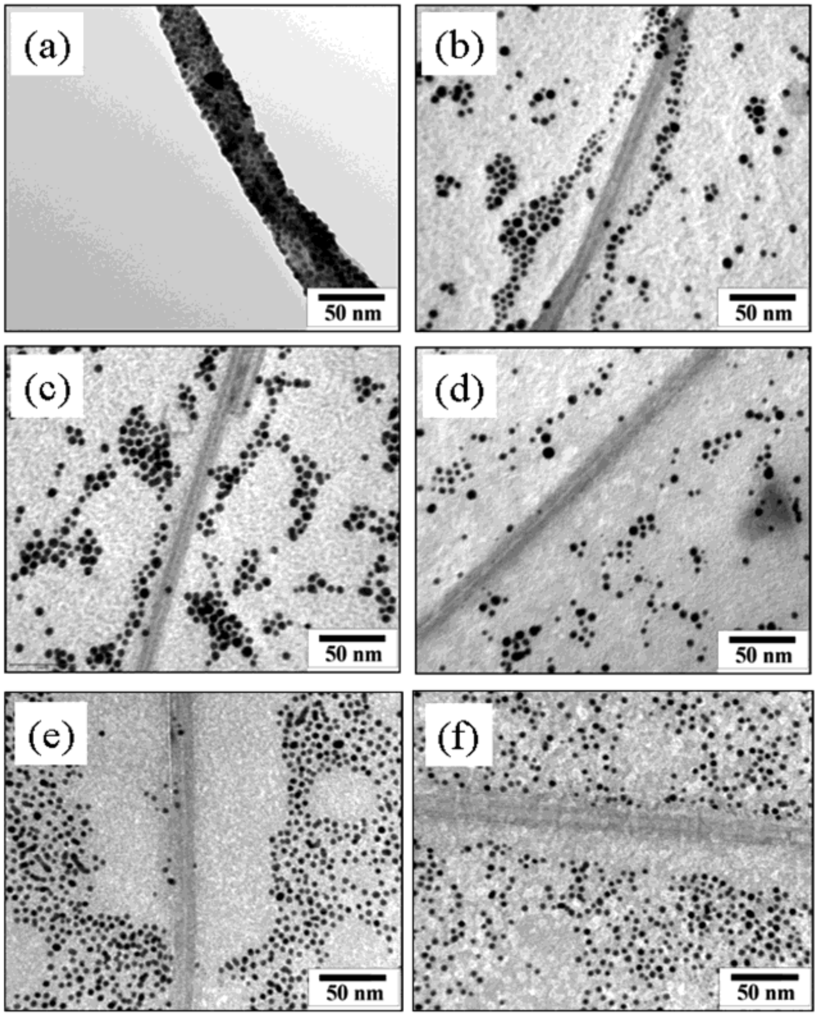


Figure 3. Transmission electron micrographs of (a) crown-modified gold nanoparticles adsorbed at the surface of a cation-modified multiwalled carbon nanotube. The same gold nanoparticles are not adsorbed at the surface of (b) a cation-precursor-modified multiwalled carbon nanotube or (c) an unmodified multiwalled carbon nanotube. Similarly, (d) thiol-modified gold nanoparticles (prior to exchange of thiol incorporating) are not adsorbed at a cation-modified multiwalled carbon nanotube. Crown-modified gold nanoparticles are not adsorbed at the surface of cation-modified multiwalled carbon nanotubes in the presence of (e) free cation or (f) free crown in solution.

for 24 h no black precipitate was observed. TEM analysis revealed no gold nanowire formation (Figure 3d).

A further series of control experiments was also performed under similar conditions. A dispersion of crown-modified gold nanoparticles (0.2 mL, 4×10^{12} nanoparticles mL^{-1}) in chloroform was added to a freshly sonicated suspension of cation-modified MWNTs (0.66 mL, 11×10^{-5} g mL^{-1}) also in chloroform, in the presence of an excess of free cation (dibenzylammonium hexafluorophosphoric acid, 3.3×10^{-3} g, 9.5×10^{-6} mol). Following equilibration of this suspension for 24 h no black precipitate was observed. TEM analysis revealed no gold nanowire formation (Figure 3e).

Also, a dispersion of crown-modified gold nanoparticles (0.2 mL, 4×10^{12} nanoparticles mL^{-1}) in chloroform was added to a freshly sonicated suspension of cation-modified MWNTs (0.66 mL, 11×10^{-5} g mL^{-1}) also in chloroform, in the presence of an excess of free crown (dibenzo24-crown-8, 4.3×10^{-3} g, 9.5×10^{-6} mol). Following equilibration of this suspension for 24 h no black precipitate was observed. TEM analysis revealed no gold nanowire formation (Figure 3f).

It is clear from these findings that MWNT-templated self-assembly of a gold nanowire is observed only when uncomplexed cation is present on the surface of the MWNTs and uncomplexed crown is present at the surface of the gold nanoparticle. On this basis it may be concluded that the templated self-assembly of nanowires is driven by formation of the surface-confined pseudorotaxane shown in Scheme 1.

The fact that coverage of the MWNT by the adsorbed gold nanoparticles is complete would suggest that the coverage of cation at the surface of the cation-modified MWNTs is extensive. It is estimated that each molecule adsorbed at the surface of a cation-modified MWNT occupies an area of 6.1×6.1 Å.[9] On the basis that the projected area of a crown-modified nanoparticle within 15 Å (the length of an adsorbed cation) of the MWNT is 1461 Å^2, it is further estimated that each particle is in contact with up to 40 cations, consistent with the high degree of coverage observed.

The possibility that the driving force for the templated nanowire assembly is charge transfer from the crown-modified nanoparticle to the cation-modified MWNT can be excluded. This assertion is supported by the findings that there is no adsorption of crown-modified gold nanoparticles at cation-precursor-modified MWNTs or cation-modified MWNTs in the presence of added crown, both of which would be expected to exhibit similar degrees of steric hindrance to cation-modified MWNTs.

Conclusions

This paper describes the use of a dibenzylammonium-cation-modified multiwalled carbon nanotube to template the noncovalent self-assembly of a gold nanowire in solution from dibenzo[24]crown-8-modified gold nanoparticles. The driving force for self-assembly is formation of a surface-confined pseudorotaxane.

By exploiting these capabilities and insights, allied to those recently reported in relation to the patterning of nanoparticles[14,17] and those that will be reported in relation to the carbon-nanotube-templated self-assembly of other nanoparticles,[18] it ought be possible to pattern nanotubes by the adsorption of a range of nanoparticles. This, in turn, will offer the prospect of diverse nanoscale components for which many applications can be foreseen.

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(17) (a) Nagle, L.; Ryan, D.; Cobbe, S.; Fitzmaurice, D. *Nano Lett.* **2003**, *3*, 51. (b) Nagle, L.; Fitzmaurice, D. *Adv. Mater.* **2003**, *15*, 933. (c) Ryan, D.; Nagle, L.; Cobbe, S.; Fitzmaurice, D. International PCT Application, 2002, application PCT/IE 02/00120.

(18) Sainsbury, T.; Fitzmaurice, D. unpublished findings.