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Directly observed covalent coupling of quantum dots to single-wall carbon nanotubes†

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Carboxylate chemistry is used to covalently couple metal nanoparticles to defect sites in controllably oxidized single-walled carbon nanotube termini and side-walls, and this process monitored by atomic force microscopy.

The broad potential of carbon nanotubes, and in particular single-wall nanotubes (SWNTs) in new generation materials, has been widely discussed and has generated much interest.[1] Their impressive mechanical and electronic properties have opened the way for the development of new nanotechnologies. If these structures are to have applicability in future electronic devices, existing fabrication methods, which generate mixtures of metallic and semiconducting nanotubes, will have to be modified. Alternatively, reliable subsequent physical or chemical control of tube properties must be achieved. To date, nanotubes have been modified using a variety of methods. Non-covalent modifications of SWNTs have been achieved by, for example, polymer wrapping[2] or ionic functionalization[3] and have been shown to increase the solubility of SWNTs in polar solvents. Biomolecules have been immobilized inside[4] nanotubes or covalently attached to pi-stacked molecules covering a nanotube surface.[5]

Metal-nanotube interactions are of considerable importance in the development of low resistance Ohmic contacts to these structures. Such interactions are essential for their reliable electrical characterization and, subsequently, application in nanoelectronics. Nanometre-scale metal clusters, stabilized on carbon, are, additionally, of considerable catalytic promise.[6] In this communication, we demonstrate a chemically-controlled nanoparticle modification of single-walled carbon nanotubes. Carboxylic acid and other oxygen-containing functionalities can be introduced to carbon nanotubes by various oxidizing treatments. Particularly popular methods have included sonication in nitric and sulfuric acids,[7] refluxing in nitric acid,[7] ozonolysis,[8] and oxidation in air.[9] The presence of carboxylate functionalities has been verified by IR spectroscopy.[8] Interestingly, by measuring the evolution of CO_2 (g) and CO (g) upon heating an HNO_3 oxidized SWNT sample to 1273 K it has been suggested that the number of carboxylic acid groups present on a carbon nanotube exceeds that expected for end group functionalization alone.[8]

We have found that the production of metal nanoparticles by decomposition of organometallic complexes can be templated by SWNTs (Fig. 1). Though comparisons between oxidized[10] and native samples support the importance of oxygen-containing (and therefore defective) tube sites in nucleating the deposition, this is somewhat difficult to demonstrate unambiguously without the active, specific, utilization of carboxylate chemistry. Most covalent functionalizations of nanotubes have utilized these carboxylic acid functional groups. A small number of sidewall functionalizations, namely fluorinations[11] and reaction with carbenes,[12] have been performed on carbon nanotubes but have been characterized only in bulk. Scheme 1 illustrates our functionalization procedure. Carboxylic acid groups on a SWNT are converted to amides by reaction with carbodiimide reagents (DCC or EDC) and 2-aminoethanethiol. The introduced thiol functionality is consequently labelled with well-defined (a distribution centred at 3.8 nm as determined by AFM) dispersed gold colloids. Herein, we report direct observations as evidence for covalent chemical functionalization of SWNTs. By imaging the same individual nanotubes with AFM before and after reaction,[13] we have observed the attachment of gold colloids to SWNT sidewalls. Contrasting reactions of oxidized SWNTs to control samples strongly suggest that colloids have been covalently attached to SWNT carboxylic acid groups *via* 2-aminoethanethiol linkages. We compare a number of oxidizing treatments of SWNTs based on results of attempted gold colloid attachment.

Fig. 2 shows typical AFM pictures of purified[14] SWNTs refluxed in 3 M nitric acid and then functionalized with gold colloids, using a thiol linker, as outlined in Scheme 1.[15] Imaging of the same SWNTs before and after reaction allowed (Fig. 3)

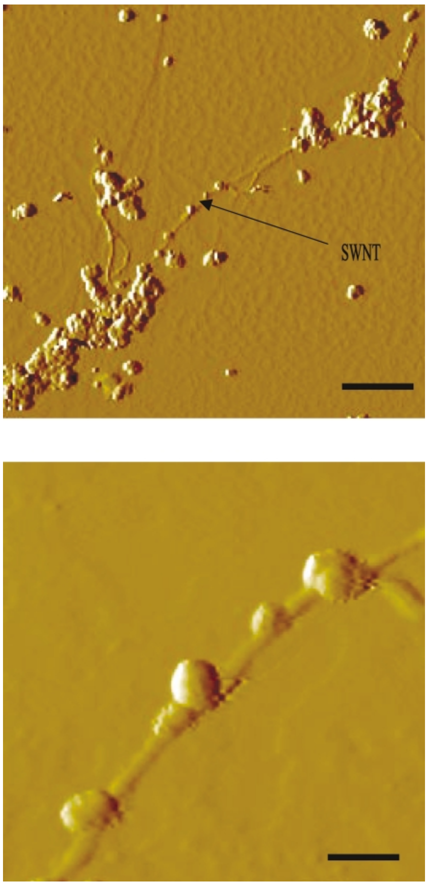

Fig. 1 Amplitude (error) tapping AFM image of a SWNT on which silver clusters have been grown by the decomposition of (cycloocta-1,5-diene-)(hexafluoroacetylacetonato)silver(I). Clusters which are not attached to the tubes presumably work themselves free during the process of sample dispersion across the substrate. Scale bars 1 µm (top) and 200 nm (bottom).

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† Electronic supplementary information (ESI) available: TEM image of SWNTs decorated with silver colloids, and energy dispersive X-ray (EDX) spectrum. See http://www.rsc.org/suppdata/cc/b1/b110690b/

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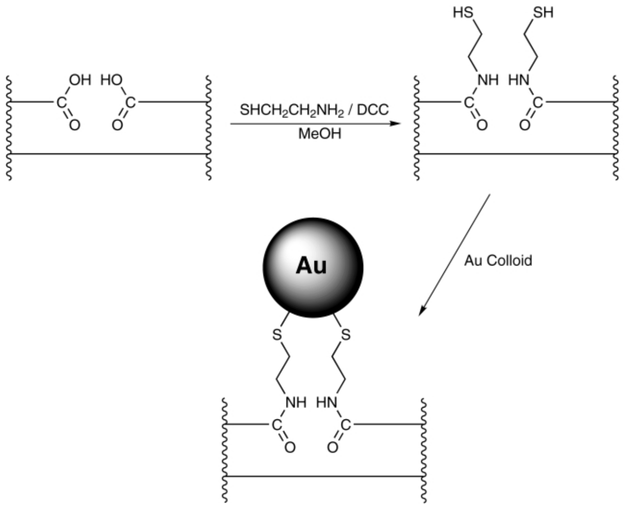
definitive differentiation of gold colloids introduced in the functionalization from metal catalyst particles present in unreacted SWNT samples and further allowed a refinement of the procedure used in nanotube activation. Comparing reactions of nitric acid refluxed tubes with controls suggests covalent chemical attachment of gold colloids. In reactions carried out with non-oxidised or vacuum annealed (1273 K) purified SWNTs, neither expected to contain carboxylic acid functionalities,[7,8] no colloid attachment was observed. Similarly, nitric acid refluxed tubes exposed to a colloid solution, without prior 2-aminoethanethiol functionalization, were not functionalized. Colloids were bound only when refluxed tubes were first treated with DCC and 2-aminoethanethiol. This presents strong evidence for covalent functionalization. By varying the oxidation procedure, it is possible to control the degree of tube wall functionalization; stirring in 3 M nitric acid or sonication in 6 M sulfuric and nitric acids, for example, was found to lead to a markedly lower degree of nanoparticle labelling.



Scheme 1 Schematic representation of the chemistry used to tether gold colloidal nanoparticles to oxidized SWNT defect sites.

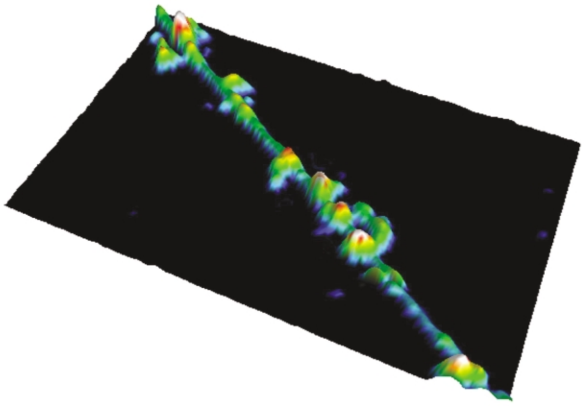


Fig. 2 Three-dimensional topographic representation of a single SWNT covalently 'decorated' with gold nanoparticles 2–3 nm in diameter. The image is approximately 50 × 150 nm in size (z scale 0–3.5 nm).

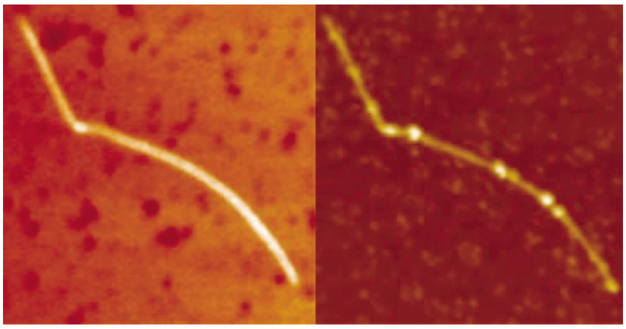


Fig. 3 Comparison of a SWNT as imaged before (left) and after (right) exposure to the coupling reagents and colloidal gold particles. Note, in particular, the appearance of particles approximately 3 nm high at positions along the tube initially 'clean.' The small particulate matter present in the right hand side image originates from exposure of the mica substrate surface to the coupling reagents and is considerably smaller in size (< 1 nm) than the metal nanoparticles. The images are 450 × 450 nm, z scale 0–4 nm.

Significantly, gold colloids were observed most often along the sides of nitric acid refluxed and gold colloid functionalized SWNTs, not only at SWNT ends. By labelling the nanotube carboxylate groups in this way, subsequent imaging gives a statistical distribution of functionalization on the nanotube. It is not known, however, whether refluxing in acid creates new defect sites along the sides of tubes or merely oxidizes defect sites already present in the walls of the SWNTs.

In summary, we have demonstrated, by AFM, a controllable 'activation' and covalent functionalization of purified SWNTs by chemically tagging with gold colloids. This method of reacting and imaging individual SWNTs on surfaces can be readily extended to test easily and unambiguously the functionalization of SWNTs with a range of groups. Further studies are currently underway to examine the effect of chemical functionalization on the electronic properties of carbon nanotubes.

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10 HiPco SWNTs (purchased from Carbon Nanotechnologies Inc., USA) were oxidized by the following three procedures. 1) Refluxing in nitric acid: 20 mg of purified HiPco SWNTs were refluxed for 12 h in 20 mL of 3 M nitric acid at 120 °C. 2) Stirring in nitric acid: 10 mg of purified HiPco SWNTs were stirred for 12 h in 20 mL of 3 M nitric acid at rt. 3) Sonication in sulfuric and nitric acids: 10 mg of purified HiPco SWNTs were sonicated for 1 h in 20 mL of a 3:1 mixture by volume of 6 M sulfuric and 6 M nitric acids.
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13 SWNTs were sonicated in 1,2-dichloroethane, spin coated onto mica and imaged in Tapping-mode AFM with a Nanoscope IIIa system (Digital Instruments).
14 HiPco SWNTs were purified according to a procedure recommended by Carbon Nanotechnologies Inc.
15 SWNT-coated mica substrates were submersed for 1–4 h in a methanol solution of 2-aminoethanethiol and DCC and washed with methanol. A few drops of 5 nm (AFM mean 3.8 nm) gold colloid solution (Sigma), diluted as desired with HPLC grade water (*ca.* 99:1), were placed on the mica surface and left for 5 min. The sample was then rinsed with methanol and dried.