# Covalent decoration of multi-walled carbon nanotubes with silica nanoparticles

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**We describe a novel tunable approach for the synthesis of carbon nanotube–silica nanobead composites. The control of nanotube morphology and bead size coupled with the versatility of silica chemistry makes these structures an excellent platform for the development of biosensors, or for optical, magnetic and catalytic applications.**

Nanomaterials are being developed for medical and biotechnological applications including gene delivery,[1] drug delivery,[2] enzyme immobilization[3] and biosensing.[4] The most commonly used materials are gold,[5] silica and semiconductors. Silica nanoparticles have been widely used for biosensing and catalytic applications due to their large surface area-to-volume ratio, straightforward manufacture, and the compatibility of silica chemistry with covalent coupling of biomolecules.[6] A key challenge in nanotechnology is the more precise control of nanoparticle assembly for the engineering of particles with the desired physical and chemical properties. Much research is currently focused on carbon nanotubes (CNT) as a promising material for the assembly of nanodevices. CNT have several unique properties, including physical strength, chemical stability, and electronic conductivity. Several laboratories are now working on new CNT–composite materials, such as CNT with a thin surface cover[7] or CNT bound to nanoparticles,[8] in order to tailor their properties for specific applications.

Here, we present the tunable synthesis of multi-walled CNT–silica nanoparticle composite materials. Instead of coupling prefabricated silica nanobeads to CNT, we chose to grow the silica nanobeads directly onto functionalized multi-walled CNT by reaction of tetraethyl- or tetramethyl-orthosilicate (TEOS or TMOS) with a functionalized CNT precursor, prepared by coupling aminopropyltriethoxysilane (APTEOS) to a functionalized multi-walled CNT through a carboxamide bond, using a water-in-oil microemulsion to strictly control nanobead size.

The body of the ideal multi-walled CNT is formed by several nested and straight cylindrical graphene sheets. In reality, nanotubes usually appear curved and have topological defects. Under strong oxidizing conditions (conc. $HNO_3$), nanotubes can be cut into shorter and straighter pieces having carboxylic acid groups at both their tips and at imperfections on their walls.[9] We oxidized multi-walled CNT with outer diameters of *ca.* 20–40 nm and lengths of 5–10 μm (NanoLab, Inc., Newton, MA, USA) (Fig. 1a) by refluxing in conc. $HNO_3$ for 6 h, followed by several washes with distilled water. The oxidized CNT (CNT-COOH) were shorter and straighter (Fig. 1b). Their carboxylic acid groups greatly facilitated their dispersion in aqueous solutions, as well as their further functionalization (Fig. 2a).

The activated CNT precursor (CNT-APTEOS) to the composite was generated from CNT-COOH by activation of its carboxylic acid groups with *N,N′*-dicyclohexylcarbodiimide (DCC) in *N*-methylpyrrolidone (NMP) to acyl isourea groups, followed by reaction with APTEOS to introduce the carboxamide-tethered triethoxysilane groups.

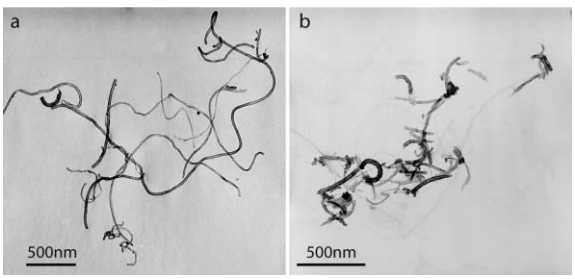


**Fig. 1** Multi-walled carbon nanotubes before (a) and after (b) oxidation in nitric acid.

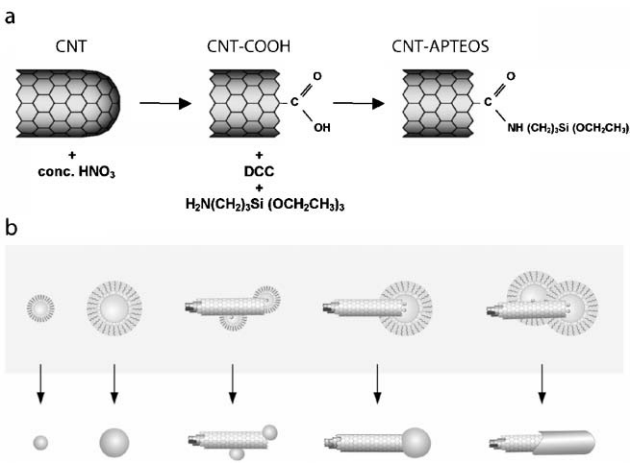


**Fig. 2** Scheme for preparing the CNT–nanoparticle composite. (a) Oxidation and preparation of the CNT-APTEOS precursor. (b) Formation of silica nanobeads in reverse micelles in a water-in-oil microemulsion. Inclusion of CNT-APTEOS nucleates the formation of nanobeads on the covalently linked propyltriethoxysilane groups (dots inside the micelles) by reaction with TEOS or TMOS.

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Briefly, 5 mg of anhydrous CNT-COOH were dispersed in 20 ml of dimethylformamide (DMF) and sonicated for 1 h before 1.1 ml of APTEOS and 10 ml of 1 M DCC in NMP were added. This mixture was sonicated for 72 h at 40 °C, then washed several times with DMF followed by ethanol. Procedures were conducted at room temperature under argon. CNT-APTEOS was collected by filtration and dried under vacuum.

CNT-APTEOS dispersed in distilled water (1.0 mg $ml^{-1}$) was added drop-wise under continuous sonication to a cyclohexane, Triton X-100, *n*-hexanol (4 : 1 : 1) microemulsion (20 ml) with waiting after each addition to ensure that a clear solution was obtained. TMOS or TEOS, to generate small or large silica nanoparticles, respectively, was added to the microemulsion, which was then sonicated for 1 h to cause the tetraalkylorthosilicate to diffuse into the aqueous core of the reversed micellar droplets in the region of the triethoxysilane groups on CNT-APTEOS (Fig. 2b). Next, catalyst (28% $NH_3$ in water) was added to the microemulsion to initiate hydrolysis and condensation of alkoxide groups, and the mixture was sonicated for 24 h at 30 °C. The nanotube–nanoparticle composite was precipitated by the addition of acetone, washed several times with water and methanol and filtered (600 nm-pore polycarbonate, Millipore). For electron microscopy, a drop of a dispersion of nanoparticles in methanol was allowed to evaporate on a 300-mesh copper grid, which had been coated with a lacey carbon film (TedPella, Inc.).

Using these procedures, we obtained new CNT–nanocomposites consisting of CNT with covalently attached silica nanobeads (Fig. 3). Non-oxidized CNT (with negligible COOH content) did not support any composite formation (not shown). The inverse microemulsion system resulted in nanobeads covalently linked to the CNT only at locations functionalized with triethoxy-silane groups, while the bare graphitic wall of the pristine CNT did not associate with reverse micelles. Transmission electron microscopic (TEM) images revealed morphologies indicative of different nanobead diameters. Small nanoparticles were found to decorate the walls and ends of the CNT prepared using TMOS as precursor (Fig. 3a–c). In many cases, small nanoparticle aggregates were observed to be associated with the CNT (Fig. 3c), as expected for the high density of functional groups on the CNT. Under the conditions used for synthesis of larger nanoparticles, CNT were either decorated by individual nanobeads (Fig. 3d–f) or had a uniform silica coating around the entire CNT (Fig. 3g and h).

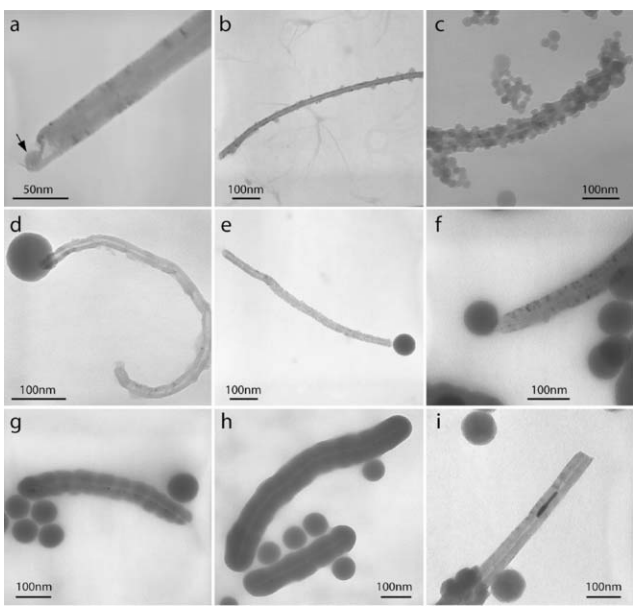


**Fig. 3** TEM images of the CNT–nanocomposites prepared using conditions for small (a–c) or large (d–i) silica nanobeads. The arrow in panel (a) indicates a nanobead at the tip of the CNT. The arrow in panel (i) indicates a polymerized silica inside a CNT.

**Table 1** Parameters for the preparation of the nanotubes-beads composite

| Nanoparticle size | *w* | *h* | *n* | Precursor |
|---|---|---|---|---|
| Large (82 ± 5 nm) | 10 | 67 | 1.7 | TEOS |
| Small (23 ± 2 nm) | 8.6 | 80 | 1 | TMOS |

We also observed some functionalized CNT that appeared to have silica within their tubes (Fig. 3i). The internal presence of silica was not observed with the non-treated nanotubes. Further work is in progress to better understand the filling mechanism.

In conclusion, we covalently coated carbon nanotubes with silica nanoparticles of different sizes. Perhaps, the most valuable feature of this work is that the architecture of the obtained assemblies can be largely controlled by varying the conditions in the synthesis. Thus, the length of CNT is regulated by the oxidation time (Fig. 1) and the size of the nanobeads by using microemulsion conditions that yield micelles of a particular size.† Because the chemical properties of the silica surface are particularly versatile and silica can be doped with fluorescent,[10] magnetic[11] or biological macromolecules,[12] nanostructures with a wide range of morphologies suitable for different applications can be obtained. We anticipate that further refinement of our water-in-oil microemulsion approach for creating novel nanostructures combined with procedures for isolating discrete products will allow us to combine different nanostructures into higher order assemblies that could be useful for a variety of applications, including providing an interface between living cells and biosensor arrays.

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## Notes and references

† Silica nanobeads were prepared in a water-in-oil microemulsion system in which the water droplets served as nanoreactors.[13] The size of the final nanospheres was mainly regulated by the dimension of the water droplets, and, therefore, by the molar ratio of water to surfactant (*w*). Smaller nanobeads were prepared by reducing *w*. Furthermore, the dimension of the final product can be controlled by varying the molar ratio of water to precursor (*h*), the molar ratio of precursor to catalyst (*n*), by choosing the reactivity of the precursor, and the reaction time and temperature. The values of the variable parameters used are presented in Table 1.

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