Dispersion of Pristine Single-walled Carbon Nanotubes in Water by a Thiolated Organosilane: Application in Supramolecular Nanoassemblies

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We report a novel technique to disperse pristine single-walled carbon nanotubes in water by ultrasonication in the presence of a thiolated organosilane and subsequent ultracentrifugation. As revealed by the sharp features in the visible range of the absorption spectrum and by transmission electron microscopy, the collected supernatant fraction was composed of small bundles of nanotubes coated by a thin layer of organosilane molecules. We hypothesized and demonstrated that the organosilane adsorbed onto the nanotubes through the thiol group leaving the silane group extruding out. The pristine properties of the nanotubes and the versatile chemistry available for sol−gel materials make the reported dispersed nanotubes an excellent scaffold for the realization of supramolecular nanoassemblies suitable for different applications. As examples, we decorated them with silica nanobeads, by using a water-in-oil nanoemulsion system, and with gold nanoparticles, by a previous derivatization with a second layer of thiolated organosilane providing exposed thiol groups.

Carbon nanotubes (NTs) are recently discovered carbonaceous materials that have gained increasing scientific interest for their extraordinary physical, chemical, and mechanical properties.[1] Their covalent or noncovalent functionalization with molecules and nanoparticles may permit their application in a wide range of fields overcoming some limitations of pristine NT, like poor solubility and tendency to aggregate in aqueous environments,[2] their absence of fluorescence in the visible range,[3] or their potential toxicity.[4]

Nondestructive silylation of NT, by using organosilanes terminated by functional groups that adsorb onto the sidewalls of the NT, has attracted recent interest for the possibility of combining the properties of pristine NT and the chemistry available for sol−gel materials. Smalley showed that single-walled carbon nanotubes (SWNTs) dispersed in dimethylformamide were able to adsorb onto $-NH_2$ functionalized silica surface but not onto a $-CH_3$ functionalized one.[5] Liu reported the silylation of SWNT through the adsorption of amino-terminated organosilane dispersed in ethanol.[6] In this letter, we report the dispersion of SWNT in pure water by ultrasonication in the presence of a thiolated organosilane, mercaptopropyl trimethoxysilane (mptmos). We observed that after ultrasoni-

cation and subsequent ultracentrifugation the collected supernatant fraction was mainly composed of small bundles of pristine SWNT coated by a thin and uniform layer of organosilane (Figure 1A). Recently, Saniger reported the deposition of gold nanoparticles (GNs) onto multiwalled carbon nanotubes (MWNTs) functionalized with aliphatic bifunctional thiols, hypothesizing that the latter reacted with the defective pentagonal sites present on the sidewalls of the NT.[7] We hypothesized and demonstrated that mptmos was able to adsorb onto the entire SWNT sidewalls through the thiol group leaving the trimethoxy- (or trihydroxy-posthydrolysis) silane group extruding out from the NT.

The exposed functional groups can offer flexible ways for the realization of NT-based supramolecular nanoassemblies by utilizing the chemistry available for sol−gel materials.[8] As examples, we reported the decoration of the dispersed SWNT (dSWNT) with silica nanobeads (SNB) (Figure 1B) and GN (Figure 1C), further demonstrating the way in which the organosilane adsorbed onto SWNT and the excellent versatility of the material.

Pristine SWNT, which were purchased from Carbon Solutions, Inc. (Riverside, CA), were approximately 1.4 nm in diameter and 500 to 1500 nm long. Distilled water (10 mL) was degassed by bubbling N_2 for 1 h and then SWNT (1 mg) and mptmos (100 μL) were added. The mixture was sonicated (model 3510, Branson Ultrasonic Corp., Danbury, CT) at 25 °C for 30 min under N_2 atmosphere and then centrifuged (Centrifuge 5417R, Eppendorf AG, Hamburg, Germany) for 15 min at 22 000 *g*. The collected clear, brownish supernatant fraction was dialyzed against distilled and degassed water, then

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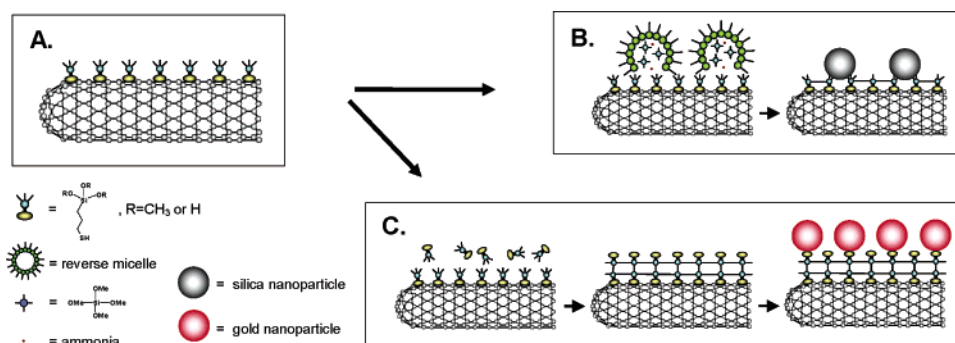
Figure 1. Dispersion of pristine SWNTs by a thiolated organosilane and realization of supramolecular nanoassemblies: (A) SWNTs were dispersed in water by mercaptopropyl trimethoxysilane that adsorbed onto the sidewalls of the nanotubes through the thiol group leaving exposed the trimethoxy-(or trihydroxy-) silane group; (B) silica nanoparticles were directly grown onto the sidewall of the functionalized SWNT by a water-in-oil nanoemulsion system; (C) gold nanoparticles were linked to the thiol groups extruding out of the SWNT sidewalls after derivatization with a second layer of mptmos. Nanotubes, gold and silica nanoparticles, and the other molecules are not shown to scale.
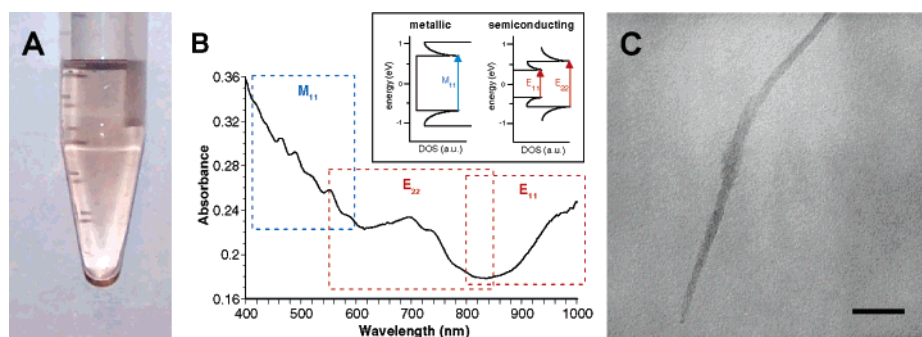
Figure 2. (A) Photograph of the supernatant fraction collected after ultracentrifugation (1 h at 100 000 g) of pristine SWNTs ultrasonicated in degassed water in the presence of a thiolated organosilane. (B) Absorption spectrum of the collected supernate. The regions of the spectrum corresponding to the electronic transitions for metallic (M_{11}) and semiconducting (E_{11} and E_{22}) SWNTs are indicated with blue and red dashed frames, respectively. The corresponding densities of states (DOS) are schematically drawn in the inset.[9] (C) TEM image of a fiberlike structure present in the supernate (scale bar 50 nm).

ultracentrifuged (Beckman Optima XL-80K Ultracentrifuge, Palo Alto, CA) for 1 h at 100 000 g. The slightly colored supernatant fraction was carefully collected and stored under N_2.

UV−vis absorbance (model 8453, Agilent Technologies, Palo Alto, CA) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) (Satellite 1000 Mid Infrared FTIR, Mattson Instruments, Madison, WI) spectroscopies were used for characterization. For transmission electron microscope (TEM) imaging, a drop of dSWNT dispersion in ethanol was allowed to evaporate on the lacey carbon film covering a 300-mesh copper grid (Tedpella, Inc., Redding, CA). TEM images were obtained using a Hitachi H-600A (Tokyo, Japan).

After ultrasonication of an aqueous dispersion of SWNT (100 μg/mL) in the presence of mptmos and brief sonication (15 min at 22 000 g), the collected colored supernate contained approximately 30 μg/mL of SWNT. Dialysis and subsequent ultracentrifugation (1 h at 100 000 g) gave a clear, slightly colored supernate that was stable, did not show any sedimentation after several months, and contained approximately 12 μg/mL of SWNT (Figure 2A). The absorbance spectrum of the supernate collected after brief centrifugation exhibited broad peaks in the visible range corresponding to the electronic transitions between the van Hove singularities of metallic (M_{11}) and semiconducting (E_{11} and E_{22}) SWNT (data not shown). Those peaks were more defined and sharper in the absorbance spectrum of the supernatant fraction collected after ultracentrifugation (Figure 2B).[9] TEM images of the dispersion immediately after the dialysis showed the presence of fiberlike material with diameters ranging from a few nanometers to 50 nm and several micrometers long. After ultracentrifugation, the

larger fibers were sedimented leaving monodispersed thin and uniform fiberlike material, less than 10 nm in diameter and 500 to 1500 nm long, in the supernatant (Figure 2C).

These results suggested that the supernatant fraction, collected after mptmos-assisted ultrasonication and subsequent ultracentrifugation, was composed of small bundles of pristine SWNT coated with a uniform layer of mptmos molecules and stably dispersed in water.

To better understand the way in which mptmos adsorbed onto SWNT sidewalls, we tried to disperse SWNT in water by ultrasonication and subsequent brief centrifugation (15 min at 22 000 g) in the presence of either aminopropyl trimethoxysilane (aptmos) or tetramethoxy orthosilicate (TMOS). In the first case, the collected supernate was clear indicating the absence of nanotubes. In the second case, we collected a very slightly colored supernate which exhibited an absorption spectrum without well-defined features in the visible range.[9] TEM images showed that it was composed of highly aggregated NT coated by a nonuniform silica layer (data not shown). We obtained the same results by varying the time and power of ultrasonication. These results suggested that mptmos hydrophobically adsorbed onto SWNT through the thiol group and not through the methoxy- (or hydroxy-) group, since the latter were also present in aptmos and TMOS.

The presence of dispersed small bundles of SWNT suggested mptmos molecules coated the sidewall of the NT. Moreover, mild ultrasonication is incapable of introducing new defective sites on the pristine sidewall of the NT. Therefore, we believe mptmos adsorbed through the lipophilic thiol group onto the whole sidewall of the NT, and not only at defective sites, as hypothesized by Saniger.[7]

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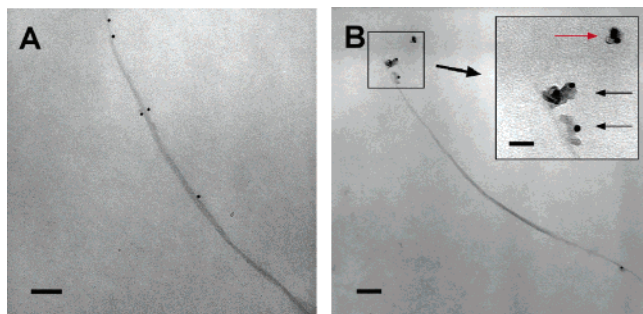
Figure 3. (A and B) TEM images of dSWNTs after incubation with colloidal gold nanoparticles (scale bars 100 nm). A few nanoparticles were observed to decorate the sidewalls of the nanotubes suggesting that the thiolated organosilane adsorbed onto the SWNT through the thiol group leaving exposed the trimethoxy- (or trihydroxy-) silane group. (B (inset)) Gold nanoparticles linked on silica nanoclusters freely dispersed on the grid (red arrow) and on dSWNT (black arrows) (scale bar 40 nm).

To further prove the orientation of mptmos adsorbed onto SWNTs, we probed the presence of exposed free thiol groups by incubating dSWNTs with colloidal GNs. The mixture was shaken at room temperature for 24 h, filtered through a 0.4 μm polycarbonate membrane (Poretics Corp., GE Osmonics Lab-store, Minnetonka, MN) and washed 5 times with water. TEM images showed dSWNTs scarcely decorated with GNs (Figure 3), indicating that very few free thiol groups extruded out from the dSWNT sidewalls. GNs were also observed to coat nonuniform silica clusters, having lateral dimension smaller than 100 nm, which were found to be freely dispersed on the TEM grid or linked to dSWNT (Figure 3B (inset)). The number of GNs decorating the dSWNT sidewalls, the amount of silica clusters, and the dimension of dSWNTs increased with both time and power of ultrasonication (higher power was obtained using a cup horn sonicator). Further, brief ultrasonication led to a very slightly colored supernatant fraction. These results are consistent with the idea that ultrasonication of a bundle of SWNTs produces local shear that partially divides the end of the rope in individual NTs or in aggregates of a few NTs. Organosilane molecules in the solution adsorb onto the isolated ends through the thiol group leaving the trimethoxysilane group extruding out. Since ultrasonication creates a gradient of

temperature inside the solution, it catalyzes the hydrolysis of (both free and adsorbed) mptmos. The trihydroxysilane groups of hydrolyzed adsorbed mptmos make the ends more hydrophilic which decreases the side-by-side van der Waals interactions between the NT of the rope and facilitates the exfoliation (unbundling) process. Therefore, ultrasonication must be prolonged and powerful enough to let the mptmos to adsorb and hydrolyze onto the NT sidewalls during their exfoliation. On the other hand, too prolonged and/or powerful ultrasonication could catalyze the condensation between free mptmos molecules and those adsorbed onto SWNTs, the condensation of free silica precursor to form clusters (which can eventually link to dSWNT), and the interlink between two (or more) mptmos-coated small bundles of NTs resulting in larger fiberlike structures. We found that sonication in a water bath for 20−30 min was optimal. Subsequent ultracentrifugation was a crucial step to enrich the solution with small bundles of SWNT. We found that 100 000 g for 1 h resulted in a collected supernatant fraction containing approximately 12% of the starting material as a uniform thin fiberlike material with lateral dimensions that make them useful for several applications. Increasing the speed of ultracentrifugation produced a supernatant fraction that exhibited thinner bundles but with fewer nanotubes (for example, ultracentrifugation at 125 000 g for 1 h left less than 4% of the starting NT in the supernate).

We recorded the ATR-FTIR spectrum of the dSWNT to probe the presence of superficial sulfonic groups that could be derived from the oxidation of thiol groups (caused by residual oxygen in the water used for the dialysis) and could explain the scarce decoration of dSWNTs with GNs. The absence of features in the 1100−1300 cm^{-1} suggested the absence of such functional groups (data not shown).

Finally, we investigated the possibility of using dSWNT for the realization of NT-based supramolecular nanoassemblies with SNB and GN. dSWNT were decorated with SNB as previously published (Figure 1B).[10] Briefly, dSWNTs (200 μg in 400 μL) were added dropwise under continuous sonication to a cyclohexane, Triton X-100, n-hexanol (4.2:1:1) nanoemulsion (10 mL) with waiting after each addition to ensure that a clear solution was obtained. TMOS (40 μL) was added to the nanoemulsion and sonicated for 1 h to cause the tetraalkyl
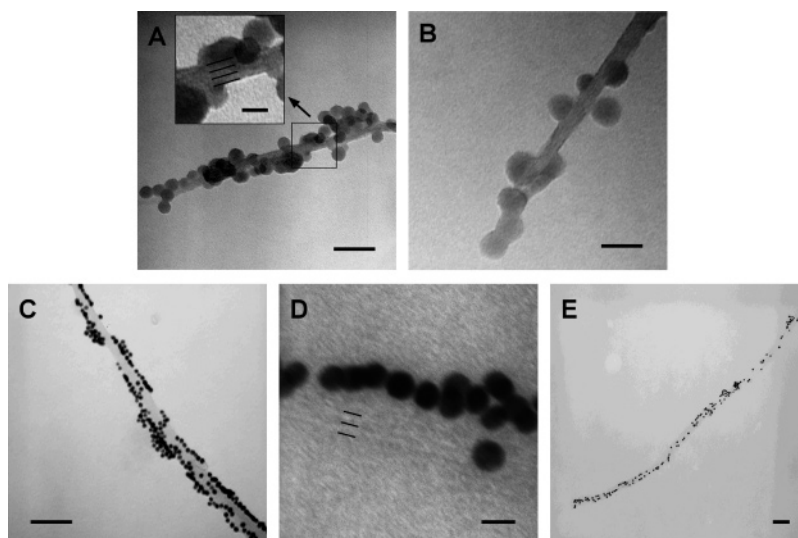
Figure 4. (A and B) TEM images of dispersed SWNTs decorated with silica nanobeads by using a water-in-oil nanoemulsion system (scale bars A, 50 nm; A (inset), 10 nm; B, 20 nm). The inset shows that the fiberlike nanostructure exhibited equally spaced striations. (C−E) TEM images of dispersed SWNTs decorated with gold nanoparticles (scale bars C, 100 nm; D, 10 nm; E, 100 nm). Approximately 3.5 nm spaced striations are evidenced in D.

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orthosilicate to diffuse into the aqueous core of the reversed micellar droplets in the region of the trimethoxy- (or trihydroxy-) silane groups on dSWNT. Next, ammonia (24 μL) was added, and the mixture was sonicated for 24 h at 20 °C. The dSWNT–SNB nanoassembly was precipitated by the addition of acetone, washed several times with water and ethanol, and filtered through a 0.4 μm polycarbonate membrane.

Further, we decorated dSWNTs with GNs (9.5 ± 0.5 nm diameter, Ted Pella, Inc., Redding, CA) by previously functionalizing the surface with thiol groups through the deposition of a second layer of mptmos onto dSWNT sidewalls (Figure 1C). dSWNTs (500 μg) were washed with ethanol (10 mL), followed by the addition of mptmos (100 μL), and sonicated for 1 h at 60 °C. During this procedure, the added mptmos and the trimethoxysilane groups on dSWNTs are hydrolyzed and covalently interlinked resulting in thiolated nanotubes. The latter were washed in ethanol and water (5 mL), and then GNs (5 mL) were added. The mixture was shaken at room temperature for 24 h. The dSWNT–GN nanoassembly was collected by filtration through a 0.4 μm polycarbonate membrane and washed 5 times with water.

TEM images exhibited supramolecular nanoassemblies composed of 13 ± 1 nm diameter silica (parts A and B of Figure 4) or gold (parts C–E of Figure 4) nanoparticles coating fiberlike structures having a diameter ranging from less than 10 to 50 nm and, frequently, showing approximately 3.5 nm equally spaced striations (Figure 4A (inset) and Figure 4D). Moreover, the fiberlike structures showing equally spaced striations were decorated by groups of perfectly aligned GNs (parts C and D of Figure 4), while those not showing the striations were decorated in a more random way (Figure 4E). These results suggested that the striations were individual SWNTs coated by a uniform (approximately) 1 nm thick layer of organosilane molecules that interlinked either during the ultrasonication process (resulting in larger fiberlike structures that were not spun down by the ultracentrifugation) or during the growth of SNB or during derivatization with the second layer of mptmos. The GNs linked to the surface of these structures following the pattern of dSWNTs, thus explaining their perfect alignment.

In conclusion, we report a novel technique to disperse SWNTs in water by ultrasonication in the presence of a thiolated organosilane with subsequent ultracentrifugation. The collected supernatant fraction was composed of thin fiberlike structures containing either bundles of a few pristine SWNTs coated by a layer of mptmos adsorbed through the thiol group or individually mptmos-coated NTs subsequently interlinked to form larger structures. The presence of the silane groups extruding out from the surface of the NTs permitted the use of the chemistry available for sol–gel materials. As examples, we decorated them with silica nanoparticles, by using a water-in-oil nanoemulsion system, and with gold nanoparticles, by previously coating the dispersed SWNTs with a second layer of mptmos to provide exposed thiol groups.

We believe these dispersed SWNTs will be an excellent scaffold for the realization of supramolecular nanoassemblies useful for a variety of applications ranging from nanoelectronics to drug delivery systems for several reasons: first, the extraordinary physical and chemical properties and the high aspect ratio of the NTs were kept intact by the nondestructive functionalization with thiolated organosilane; second, they were dispersed in water in bundles composed of few NTs; third, their surface can be easily functionalized by using the versatile chemistry available for sol–gel materials. Further work is in progress regarding the functionalization of dSWNTs with a second layer of organosilane terminated by functional groups useful to subsequently decorate the structures with biologically relevant molecules.

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(9) A SWNT is a graphene sheet rolled-up and capped at the ends with emi-fullerenes. A SWNT is metallic or semiconductor depending on its chirality (diameter and wrapping angle). The density of states (DOS) near the Fermi level (located at $E = 0$) is zero for semiconducting SWNT but is nonzero for metallic SWNT. The quasi one-dimensionality of a SWNT causes its DOS to be characterized by a series of sharp features (van Hove singularities) located at energies depending upon the reciprocal nanotube diameter (Figure 2B (inset)). Therefore, the absorption spectrum of a SWNT is expected to be composed by a series of sharp peaks corresponding to the interband electronic transitions between the van Hove singularities. The transition between the first van Hove singularities of a semiconducting SWNT has energy (E_{11}) in the ~800 to ~1600 nm wavelength range partially overlapping the ~550 to ~850 nm wavelength range of its E_{22} transition. The transition between the first van Hove singularities of a metallic SWNT has energy (M_{11}) in the ~400 to ~600 nm wavelength range (Figure 2B). Since nanotubes grow with different chiralities, the absorption spectrum of a batch of SWNTs is expected to be the superposition of distinct electronic transitions, each arising from a specific chirality. Well-defined electronic transitions are indicative of weak interactions between NTs through side-by-side van der Waals contact.[2b] Therefore, the intensity and shape of the electronic transitions in the absorption spectrum give an indication of the level of aggregation of the NT.

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