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Dispersion of pristine single-walled carbon nanotubes in water by a thiolated organosilane: application in supramolecular nanoassemblies

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Abstract

We report a novel technique to disperse pristine single-walled carbon nanotubes in water by ultrasonication in 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 (NT) are recently discovered carbonaceous materials that have gained increasing scientific interest for their extraordinary physical, chemical and mechanical properties.¹ Their covalent or non-covalent 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

Non-destructive silylation of NT, by using organosilanes terminated by functional groups that adsorb onto the sidewalls of the NT, have 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 (SWNT) dispersed in dimethylformamide were able to adsorb onto $-NH_2$ functionalized silica surface but not onto $-CH_3$ 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 presence of a thiolated organosilane, mercaptopropyl

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trimethoxysilane (mptmos). We observed that after ultrasonication 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 (GN) onto multi-walled carbon nanotubes (MWNT) 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-post-hydrolysis) 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 N₂ for 1 h and then SWNT (1 mg) and mptmos (100 μ L) were added. The mixture was sonicated (model 3510, Branson Ultrasonic Corp., Danbury, CT) at 25°C for 30 min under N₂ 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 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 N₂.

UV-Vis absorbance (model 8453, Agilent Technologies, Palo Alto, CA) and 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 μ g/mL) in presence of mptmos and brief sonication (15 min at 22000 g) the collected colored supernate contained approximately 30 μ g/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 μ g/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 (M₁₁) and semiconducting (E₁₁ and E₂₂) 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 fiber-like material with diameters ranging from a few nanometers to 50 nm and several microns long. After ultracentrifugation the larger fibers were sedimented leaving monodispersed thin and uniform fiber-like 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

22000 g) in 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 non-uniform 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

To further prove the orientation of mptmos adsorbed onto SWNT, we probed the presence of exposed free thiol groups by incubating dSWNT with colloidal GN. The mixture was shaken at room temperature for 24 hours, filtered through a 0.4- μ m polycarbonate-membrane and washed 5 times with water. TEM images showed dSWNT scarcely decorated with GN (Figures 3A and 3B), indicating that very few free thiol groups extruded out from the dSWNT sidewalls. GN were also observed to coat non-uniform 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 GN decorating the dSWNT sidewalls, the amount of silica clusters, and the dimension of dSWNT 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 SWNT produces local shear that partially divides the end of the rope in individual NT or in aggregates of a few NT. Organosilane molecules in the solution adsorb onto the isolated ends through the thiol group leaving the trimethoxy-silane group extruding out. Since ultrasonication creates gradient of temperature inside the solution, it catalyzes the hydrolysis of (both free and adsorbed) mptmos. The trihydroxy-silane 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 SWNT, 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 NT resulting in larger fiber-like 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 fiber-like 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 dSWNT in order to probe the presence of superficial sulfonic groups that could derive from the oxidation of thiol groups (caused by residual oxygen in the water used for the dialysis) and could explain the scarce decoration of dSWNT with GN.

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, dSWNT (200 μg in 400 μL) were added drop-wise 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 tetraalkylorthosilicate 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 (Poretics Corp., GE Osmonics Labstore, Minnetonka, MN).

Further, we decorated dSWNT with GN (9.5 $\pm$ 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). dSWNT (500 μg) were washed with ethanol (10 mL), followed by addition of mptmos (100 μL) and sonicated for 1 h at 60°C. During this procedure the added mptmos and the trimethoxy-silane groups on dSWNT are hydrolyzed and covalently interlinked resulting in thiolated nanotubes. The latter were washed in ethanol and water (5 mL), and then GN (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 $\pm$ 1 nm-diameter silica (Figures 4A, B) or gold (Figure 4C-E) nanoparticles coating fiber-like structures having a diameter ranging from less than 10 nm to 50 nm and, frequently, showing approximately 3.5 nm-equally spaced striations (Figure 4A (inset) and Figure 4D). Moreover, the fiber-like structures showing equally spaced striations were decorated by groups of perfectly aligned GN (Figures 4C and 4D), while those not showing the striations were decorated in a more random-way (Figure 4E). These results suggested that the striations were individual SWNT coated by a uniform (approximately) 1 nm-thick layer of organosilane molecules that interlinked either during the ultrasonication process (resulting in larger fiber-like 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 GN linked to the surface of these structures following the pattern of dSWNT, thus explaining their perfect alignment.

In conclusion, we report a novel technique to disperse SWNT in water by ultrasonication in the presence of a thiolated organo-silane with subsequent ultracentrifugation. The collected supernatant fraction was composed of thin fiber-like structures containing either bundles of few pristine SWNT coated by a layer of mptmos adsorbed through the thiol group or individually mptmos-coated NT subsequently interlinked to form larger structures. The presence of the silane groups extruding out from the surface of the NT 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 SWNT with a second layer of mptmos to provide exposed thiol groups.

We believe these dispersed SWNT 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 NT were kept intact by the non destructive functionalization with thiolated organosilane; second, they were dispersed in water in bundles composed of few NT; 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 dSWNT with a second layer of organosilane terminated by functional groups useful to subsequently decorate the structures with biologically relevant molecules.

Acknowledgements

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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- 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 SWNT 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 NT 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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Figure 1.

Dispersion of pristine SWNT by a thiolated organosilane and realization of supramolecular nanoassemblies. A: SWNT 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 SWNT ultrasonicated in degassed water in 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}) SWNT 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 fiber-like structure present in the supernate (scale bar 50 nm).

Figure 3.

A and B: TEM images of dSWNT after incubation with colloidal gold nanoparticles (scale bars 100 nm). 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).

Figure 4.

A and B. TEM images of dispersed SWNT 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 fiber-like nanostructure exhibited equally spaced striations. C-E. TEM images of dispersed SWNT decorated with gold nanoparticles (scale bars A: 100 nm, D: 10 nm, E: 100 nm). Approximately 3.5 nm-spaced striations are evidenced in D.