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Noncovalently silylated carbon nanotubes decorated with quantum dots

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Abstract

A nanoassembly of single-walled carbon nanotubes coated by a thin layer of silica followed by quantum dots was prepared. That the quantum dots retained their photoluminescent properties after deposition onto the silylated carbon nanotubes suggests that the thin layer of silica prevented the quenching of the fluorescence by the nanotubes. This fluorescent nanoassembly represents an excellent building block for photoelectric and optical devices and biological nanoprobe.

Keywords

Carbon nanotubes; Adsorption; Transmission electron microscopy; Absorption; Luminescence

Intense investigations are underway to explore the unique morphological, electronic, mechanical, thermal and optical properties of carbon nanotubes (CNTs) [1]. In many cases, to fabricate nanodevices or composites capable of taking full advantage of their unique properties, CNTs must be attached to other molecules, nanoparticles or surfaces. Semiconducting nanocrystals, also known as quantum dots (QDs), exhibit strong size-dependent optical and electrical properties. Their high luminescence yields and the potential of adjusting their emission and absorption wavelengths by selecting for nanocrystal size make QDs attractive for constructing optoelectronic devices with tailored properties or in vivo biosensing applications. QDs have been attached to CNTs by a molecular [2,3], a macromolecular [4] or a polymeric [5,6] linkers with the choice being dictated by the final application of the CNT-QD nanoassembly. For example, for biosensorial applications CNTs that are easily visualized by simple optical microscopy are useful [4-6]. Therefore, the linker used to couple QDs to the CNT sidewall must avoid the fluorescence quenching caused by their interactions with the CNTs, which could provide an alternative, non-irradiative decay path for the photoexcited electrons of the QDs. On the other hand, for CNT-based photoelectrochemical cell fabrication, the linker should permit electron transfer from the excited states of the QD (luminophore) to

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the conduction band of the CNT (quencher) [3,5]. Therefore, studying the optical properties of CNT-QD nanoassemblies would give information about the conducting properties of the linker used to link QDs to the CNT surface.

Recently, we reported a novel technique to silylate full-length single-walled (SW) CNTs by ultrasonication in the presence of a thiolated organosilane and subsequent ultracentrifugation [7]. The collected supernatant fraction was demonstrated to contain small bundles of CNTs that were coated by a thin layer of organosilane, which had adsorbed onto the CNT surface through the thiol group leaving the trimethoxy- (or trihydroxy-) silane group protruding from the composite surface (Figure 1(I)). In this letter, we report the decoration of these silylated CNTs with QDs through the deposition of a second layer of organosilane onto the silylated surface so that amino or thiol groups were exposed (Figure 1(II)) for linkage to QDs (Figure 1(III)). Photoluminescence characterization of the CNT-QD assembly gave information about the conducting properties of the thin layer of silica between CNTs and QDs.

The CNT-QD nanoassembly was fabricated by a three-step process. SWCNTs from Carbon Solutions, Inc. (Riverside, CA) were approximately 1.4-nm in diameter and 500 to 1500-nm long. ZnS-covered CdSe QDs from Evident Technologies, Inc. (Troy, NY) were capped by trioctylphosphine oxide (TOPO), had 612-nm emission wavelengths and diameter of 5.2 nm. Gold nanoparticles (GNs) from Ted Pella, Inc. (Redding, CA) had a 9.5 ± 0.5 -nm diameter. Fluorescamine, mercaptopropyl trimethoxysilane (mpts) and aminopropyl trimethoxysilane (apts) were from Sigma-Aldrich Corp. (St. Louis, MO). Adducts were characterized by UV-Vis absorbance (model 8453, Agilent Technologies, Palo Alto, CA) and fluorescence (model MOS-250, Bio-Logic, Claix, France) spectroscopies and transmission electron microscope (TEM) imaging. For the latter, a drop of nanostructure dispersion in EtOH was allowed to evaporate on the lacey carbon film covering a 300-mesh copper grid (Tedpella, Inc., Redding, CA).

In the first step, CNTs were silylated by sonication in presence of a thiolated organosilane and subsequent ultracentrifugation following our published protocol [7] with slight modifications. Distilled water (10 mL) was degassed by bubbling in N₂ for 1 h and then CNTs (2 mg) and mpts (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 10 min at 32,000 g. The collected clear brownish supernatant fraction was dialyzed against degassed and distilled H₂O, and then centrifuged for 1 h at 32,000 g. Finally, the collected supernate was ultracentrifuged (Beckman Optima™ XL-80K Ultracentrifuge, Palo Alto, CA) for 1 h at 125,000 g. The slightly brown supernatant fraction was carefully collected and stored under N₂. TEM images showed that the supernatant fraction was composed by fiber-like structures containing small bundles of CNTs coated by a thin layer of silica having a diameter less than 20 nm (Figure 2A). Frequently the fiber-like structures showed approximately 3 nm-equally spaced striations (Figure 1A (inset)). As previously observed [7], the striations could be interpreted as SWCNT (1.4 nm in diameter according to company literature) coated by a less than 1 nm-thick layer of organosilane molecules (corresponding to a single layer of molecules adsorbed onto the CNT sidewalls [8]) that probably interlinked during the ultrasonication process resulting in larger structures that were not spun down by the ultracentrifugation. The silylated CNTs (sCNTs, I in Figure 1) stably dispersed in organic as well as aqueous solvents and exhibited in the visible absorbance spectrum well defined and broad peaks corresponding to the electronic transitions between the van Hove singularities of metallic and semiconducting SWCNTs (Figure 2B) [9]. Since the intensity and shape of the electronic transitions in the absorption spectrum give an indication of the level of aggregation of the SWCNT, the recorded absorbance spectrum confirmed that the collected supernatant fraction was composed by small bundles of SWCNT (either individually or globally coated by a thin layer of silica).

In the second step, the surface of sCNTs was further functionalized with amino or thiol groups through the condensation of a layer of apts or mpts onto the sCNT sidewalls, respectively. To sCNT (500 μ g) washed 3 times in 5 mL of EtOH was added 50 μ L of organosilane (apts or mpts) and the mixture was sonicated for 15 min at 60°C. During this procedure the trimethoxy-silane groups on sCNTs and the organosilane hydrolyzed and covalently interlinked resulting in CNTs functionalized with amino or thiol groups (fCNTs, II in Figure 1). fCNTs were washed three times in EtOH/CHCl₃ (1:1) and five times in anhydrous toluene (5 mL each). The presence of amino or thiol groups protruding from the fCNT sidewalls was verified using the fluorescamine or tagging fCNTs with GNs, respectively. Amino-fCNTs (100 μ g) in 2 mL of water were mixed with 200 μ L of 5mM fluorescamine in MeOH and sonicated at room temperature for 5 min. Their intense fluorescence at 475 nm was detected using an excitation wavelength of 390 nm and was indicative of the presence of amino groups on the fCNT sidewalls. Thiol-fCNTs (200 μ g) in 2 mL of water and 1 mL of colloidal GNs were shaken at room temperature for 24 h. The mixture was filtered through a 0.4- μ m polycarbonate-membrane (Poretics Corp., GE Osmonics Labstore, Minnetonka, MN) and washed 5 times with water. TEM images exhibited fiber-like structures decorated with GNs, indicating that the fCNT sidewalls were successfully functionalized with thiol groups.

In the third step, fCNTs were decorated with QDs. TOPO was first washed from the QD surface by repeated cycles of precipitation with MeOH, centrifugation, and redispersion of the precipitate into hexane to test if all the TOPO has been washed away. QDs were finally dispersed in toluene. fCNTs (200 μ g) were mixed with 2 mL of 15 μ M of 612 nm-emitting QDs and sonicated at 80°C for 12 h. The CNT-QD nanoassembly was collected by two rounds of filtration (0.2- μ m fluoropore polytetrafluoroethylene-membrane filter, Millipore, Billerica, MA), and dispersed in toluene. TEM images of the CNT-QD showed fiber-like structures decorated with dark particles representing the QDs (Figure 2C). The absorbance spectrum in the visible range of the CNT-QD nanoassembly in toluene clearly revealed the 600 nm-centered peak arising from QDs (Figure 2 D(inset)) and the spectroscopic features arising from the electronic transitions for metallic and semiconducting CNTs (Figure 2D) [9]. In steady-state experiments, excitation of CNT-QD in toluene at 360 nm produced an emission band that was centered at 615 nm, red-shifted by 3 nm and slightly broader compared to that of the original QDs (Figure 2 E and Table 1). We obtained the same emission spectra for the nanoassemblies fabricated by functionalizing the sCNTs with either thiol or amino groups. Since TEM images revealed that no free QDs were in the dispersion, the fact that the emission profile had not considerably changed after QDs were linked onto fCNTs suggests that the CNTs only slightly affected the emission of the QDs probably because the thin silica layer between the two components of the nanoassembly (CNT and QD) avoided electron transfer and electronic tunneling from the QDs to the CNTs.

In conclusion, we have reported the fabrication of a nanoassembly of full-length single-walled carbon nanotubes coated by a thin layer of silica followed by QDs. That the latter retained their photoluminescent properties after the deposition onto the sCNTs suggests that the thin layer of silica prevented the quenching of the fluorescence by the CNTs. Therefore, the reported fluorescent nanoassembly could represent an excellent building block for photoelectric and optical devices and biological nanoprobes.

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8. Models of mpts molecule showed that the maximum distance between the thiol group and the oxygen atoms is 0.704 nm.
9. A SWCNT is a graphene sheet rolled-up to form a tiny cylinder with a diameter of few nanometers and a length of several microns. A SWCNT is metallic or semiconducting 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 SWCNTs, but is non-zero for metallic SWCNTs. The quasi one-dimensionality of a SWCNT causes its DOS to be composed by sharp features (called van Hove singularities) located at energies related to the diameter of the SWCNT (Figure 2B (inset)). The absorption spectrum of a SWCNT is expected to be characterized by a series of peaks that correspond to the interband electronic transitions between the van Hove singularities and are located in different wavelength regions for metallic and semiconducting nanotubes. Since SWCNTs grow with different chiralities, the absorption spectrum of a batch of SWCNTs is expected to be the superposition of distinct series of peaks, each arising from a specific chirality. Well defined spectroscopic features are indicative of weak interactions between CNTs. Therefore, the intensity and shape of the spectroscopic features in the absorption spectrum are indicative of the level of aggregation of the CNTs.

Fig1.

Decoration of SWCNTs with QDs. CNTs were silylated through adsorption of a thiolated organosilane (sCNT, I). Condensation of a second layer of organosilane modified the surface of CNTs with amino or thiol groups (fCNT, II) to which QDs were linked (CNT-QD, III).

Fig 2.

A: TEM image of a fiber-like structure present in the supernate collected after sonication of SWCNTs in presence of a thiolated organosilane then ultracentrifuged (100-nm scale bar). The inset shows a TEM image of an approximately 12 nm-in-diameter fiber-like nanostructure exhibiting (approximately) 3 nm-equally spaced striations (18-nm scale bar). B: Absorbance spectrum of sCNTs dispersion in toluene. The regions of the spectrum corresponding to the electronic transitions for metallic (M_{11}) and semiconducting (E_{11} and E_{22}) CNTs are indicated with solid and dotted dashed frames, respectively. The corresponding densities of states (DOS) are schematically drawn in the inset [9]. C: TEM image of amino-fCNT decorated with 612 nm-emitting QDs (50-nm scale bar). D: Absorbance spectrum of CNT-QD nanoassembly dispersion in toluene; Inset: Absorbance spectrum of 612 nm-emitting QD dispersion in toluene. E: Normalized emission spectra of 612 nm-emitting QD (dotted line) and CNT-QD nanoassembly (solid line) dispersions in toluene.

Table 1

Spectroscopic parameters, maximum emission wavelength and full-width half-maximum, for dispersions of QD and CNT-QD in toluene.

Sample	$\lambda_{\text{max}}^{\dagger}$ (nm)	FWHM(nm) [‡]
QD	612	30
CNT-QD	615	33

[†] maximum emission wavelength;

[‡] full-width half-maximum.