Covalent attachment of quantum dot on carbon nanotubes

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Abstract

The assembly of quantum dot (QD) on the surface of multi-walled carbon nanotubes (MWNT) in aqueous solution leading to QD-MWNT hybrid structures is demonstrated. The assembly of QDs on the MWNTs surface occurs through interaction of the amine groups on the MWNTs with the mercaptoacetic acid modified QDs. Furthermore, QD-MWNT hybrid material shows an excellent solubility in aqueous solution, this will be significant for its potential application in bioassay, bioconjugation, and biosensors.

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1. Introduction

Carbon nanotubes (CNTs) have been well studied in recent years due to their interesting physical properties [1,2]. Currently, a large amount of research in carbon nanotube chemistry is directed to the synthesis of diverse organic derivatives with the aim to promote surface functionalization and simultaneously provide colloidal stability to the resulting modified carbon nanotubes (CNT) in organic or aqueous media [3]. Such surface modification of CNT through covalent bonding of functional organic molecules opens the way to structural materials of high technological importance [4–9]. Recently, a new class of CNT products has been derived from the combination of CNT with metal ions [10], metals [11,12], and semiconducting nanoparticles [13,14]. This class of CNT derivatives shows promising features for nanoelectronics and other applications. Quantum dots provide a functional platform for novel materials and devices that benefit from the unique physical properties that arise from their quantum-confined nature, giving rise to properties between those of the molecular and the bulk [15–17,4,18]. For semiconductor quantum dots such as CdSe, variation of particle size provides continuous and predictable changes in fluorescence emission [19,20]. Recently, several methods have been developed to disperse QDs in aqueous media for use in biologically relevant studies [21,22]. Functionalization of the water-soluble QD surface allows the formation of QD bioconjugates that can bind specifically to target molecules and form stable conjugate complexes. As such, QDs have already been used successfully in cellular imaging, immunoassays, DNA hybridization, and optical barcoding [14,23–26].

In this Letter, a new strategy to derivatize CNT with quantum dot is described. Mercaptoacetic acid capped CdSe nanoparticles were attached to carbon nanotubes by means of an interlinker molecule – ethylenediamine. This method provides a direct route to synthesize QD-CNT composites. This offers the possibility to predefine the size, shape, and amount of the nanoparticles attached on CNTs, depending on the specific application. Immobilization of biomolecules on QD and CNT is an area of great interest. Such hybrid materials have numerous applications in the areas of biotechnology, immunosensing, and biomedical applications.
2. Experimental section

2.1. Materials

Multi-walled carbon nanotubes (MWNT) were obtained from Shenzhen Nanotech Port Co., (Shenzhen, China). CdSe nanoparticles were prepared by using X. Peng’s method. Ethylene diamine, nitric acid and sulfuric acid were purchased from Shanghai Chemical Reagent Corporation (Shanghai, China). Deionized water with nominal resistivity higher than 18.2 MΩ cm was produced by Barnstead E-Pure with a reverse osmosis system was used for all chemical procedures. All chemicals were used without further purification.

2.2. Mercaptoacetic acid coating of CdSe nanoparticles

As-synthesized CdSe quantum dots are capped with tri-octylphosphine oxide (TOPO) ligands, and thus are hydrophobic. To obtain QDs that can bind to the amine functionalized MWNTs, the TOPO must be replaced with a suitable hydrophilic ligand. The resulting CdSe QDs were functionalized MWNTs, the TOPO must be replaced with cyclophobic. To obtain QDs that can bind to the amine functionalized MWNTs that have been reacted with octylphosphine oxide (TOPO) ligands, and thus are hydrophilic.

2.2.1. Attachment of CdSe QDs to MWNT

Crude MWNTs (0.5233 g) were added to a mixture containing H2SO4/HNO3 = 3:1 (v/v). The mixture was placed in an ultrasonic bath (40 kHz) for 30 min and then stirred for 24 h while being boiled under reflux. The mixture was then vacuum-filtered through a 0.22 μm Millipore polycarbonate membrane and subsequently washed with distilled water until the pH of the filtrate was ca. 7. The filtered solid was dried under vacuum for 12 h at 60 °C, yielding MWNT-COOH (0.5036 g).

2.2.2. Preparation of MWNT-COCl from MWNT

MWNT-COOH (0.5036 g) was suspended in SOCl2 (30 ml) and stirred for 24 h at 65 °C. The solution was filtered, washed three times with anhydrous THF, and dried under vacuum at room temperature for 24 h, generating MWNT-COCl (0.4926 g).

2.5. Synthesis of MWNT-NH2 Initiators from MWNT-COCl

MWNT-COCl (0.4926 g) was mixed with ethylene diamine (20.0 ml) and placed in an ultrasonic bath (40 kHz) for 5 h at 60 °C. The mixture was stirred for another 24 h at 60 °C. The resulting solid was separated by vacuum-filtration using 0.22 μm Millipore polycarbonate membrane filter and subsequently washed with water. After repeated washing and filtration, the resulting solid was dried overnight in a vacuum, generating MWNT-NH2 (0.5042 g).

3. Attachment of CdSe QDs to MWNT

The MWNT-NH2 aqueous solution was centrifugated and redispersed in water. The mercaptoacetic acid coated QDs aqueous solution was added to the MWNTs and the mixture was sonicated at 50 °C under nitrogen for 4 h. The suspension was then cooled to room temperature, centrifugated at 8000 rpm for 30 min, and rinsed thrice with water using several cycles of centrifugation and decantation. The coupled QD-MWNTs were filtered through a 3.0 μm Teflon membrane filter and resuspended in water. The ratio of QDs to MWNTs (QD/MWNT) was varied from 10:1 to 1:10 (w/w).

4. Instrumentation and measurements

UV–vis absorption spectra were obtained on UNICAM UV 300 spectrometers (Thermo Electronic). Fourier transform infrared (FTIR) spectra were recorded using a PE Paragon 1000 spectrometer (KBr disk). The high-resolution TEM measurements were carried out using a JEOL 2010F analytical electron microscope with a field emission source. The accelerating voltage was 200 kV. Photoluminescence spectra were measured on a LS 55 Luminescence Spectrometer (Perkin–Elmer).

5. Results and discussion

5.1. TEM observation

Typical HRTEM images depicting the attachment of single CdSe QDs to MWNTs are shown in Fig. 1. As seen in Fig. 1, the TEM image of nanotubes before functionalization is devoid of any particle-like features (Fig. 1a), amine functionalized MWNTs that have been reacted with CdSe-COOH have nanoparticles connected to the nanotube sidewalls and ends, thus suggesting that functionalization of the MWNTs with QDs was successful.

We repeated the QD-MWNT coupling reactions with nanotubes synthesized using different methods, with quantum dots having CdSe diameters that ranged from 2.8 to...
4.6 nm (Fig. 1b). It is important to note that TEM indicate that most of the observed quantum dot binding to MWNTs occurs with single QDs. On the other hand, TEM images of chlorocarboxyl-functionalized MWNTs reacted with mercaptoacetic acid functionalized quantum dots do not contain any particle-like features (Fig. 1c); the individual sidewalls of each MWNT in the bundles can be seen clearly and are featureless.

The QD/MWNT mass ratio was varied from 10:1 to 1:10. We noted CdSe QD attachment to a significant portion of the nanotube sidewalls, indicating that the acid cutting process attacks not only the nanotube ends but also a remarkable percentage of the sidewalls (Fig. 1d–g). This observation is consistent with Raman studies showing that the D-band Raman intensity (the measure of sp² disorder in a nanotube) increases significantly upon acid purification of the nanotubes. This result also agrees with studies that have shown a very high percentage of acidic carbon sites on purified MWNT material. As the QD/MWNT ratio decreased, the number of attached QDs per nanotube decreased, as expected. Unreacted individual quantum dots and QD aggregates are also typically observed in the TEM images. The frequency of these observations is a function of the QD amount used for the coupling; larger amounts of QDs typically result in more free particles present in the images. While the majority of unreacted QDs should have been removed during the filtration process, this procedure retains some free particles in the final suspension.

5.2. UV–vis and photoluminescence (PL) spectra

As shown in Fig. 2, the CdSe diameter as determined from optical absorption data (Fig. 2a) correspond to the same the diameter of the CdSe nanoparticles in the TEM image (Fig. 1b). Fig. 2 shows typical absorption spectra of CdSe QDs before (Fig. 2a) and after functionalization with mercaptoacetic acid (Fig. 2b). Quantum dots capped with TOPP or mercaptoacetic acid both display a peak at 560 nm due to exciton absorption. The fact that the first exciton state does not blue shift upon ligand substitution suggests that substantial surface oxidation did not occur. The UV–vis spectra of the modified carbon nanotubes are useful not only for identification reasons but also for testing the stability of the resulting QD-MWNT aqueous
solution. Thus, aqueous solutions of the QD-MWNT derivatives were stable for at least 7 weeks without changes in their UV–vis spectra. The known absorption bands of CdSe QDs characterize the spectrum from the QD-MWNT solutions (Fig. 2c). It is worth noting that in the spectrum of the QD-MWNT (Fig. 2c), the QD absorptions are superimposed on a continuously rising background that originates from the presence of MWNTs. This background is not observed in the spectrum obtained from CdSe and CdSe-COOH (Fig. 2, curves a and b).

A comparison of photoluminescence curves that were obtained from the original QDs, the water soluble QDs,
and the MWNT-conjugated QDs (Fig. 2e–g) indicated that the optical properties of QDs remain unchanged after solubilization and conjugation. Fig. 2f also showed that the emission spectra and efficiencies were similar for the original sample (in chloroform) and the water-soluble QDs. Fig. 2g showed that the PL intensity decreased as the QD-MWNT hybrid material was formed.

5.3. FTIR spectroscopy

It is possible that the QD-MWNT complexes observed using TEM are not due to covalent attachment of individual QDs to MWNTs but rather to accidental resting of free QDs along MWNTs due to the mixing process. Therefore, FTIR was also used to confirm that individual CdSe QDs were bound to MWNTs to prove that the CdSe QDs and the MWNTs are covalently attached through an organic linkage and not through nonspecific interactions. Thus, we conclude that nonspecific QD attachment did not occur and that the attachment of the QDs functionalized with mercaptoacetic acid to individual MWNTs occurred through amide bond formation. Amine-functionalized MWNT shows a broad amine peak at 3451 cm\(^{-1}\) (Fig. 3a), indicating the presence of amine groups on the MWNT surface. Additional evidence that the QDs are capped with mercaptoacetic acid comes from infrared spectroscopy (Fig. 3b), where the presence of a strong –COOH peak at 1711 cm\(^{-1}\) indicates the desired ligand exchange occurred on the quantum dot surface. Covalent attachment between amine groups of MWNTs and carboxyl groups on QD surface is verified by pronounced amide I and II vibrational stretches (1645 and 1555 cm\(^{-1}\), respectively) in Fig. 3c spectrum and shifts in the N–H stretching region (3500–3000 cm\(^{-1}\)). Also, the –COO– stretch absorbance of mercaptoacetic acid decreases and shifts to higher wave-number at 1722 cm\(^{-1}\), indicating that there exist excess carboxyl groups after the formation of QD-MWNT hybrid materials.

6. Conclusions

The results described in this communication establish that the immobilization of QD onto MWNT surfaces has been achieved. We present a simple method for coupling individual MWNTs to single CdSe QDs. Amine groups present on the nanotube sidewalls, as well as the ends, lead to amide bond coupling with mercaptoacetic acid coated CdSe nanoparticles. QDs attached to the MWNT sidewalls and ends by HRTEM characterization. Attachment and control of the chemistry at the nanotube surface is important since this configuration could result in a bottom-up approach toward assembly of MWNTs necessary for future nanoelectronic devices. In conclusion, our results have direct implications for self-assembly of carbon nanotube nanodevices using chemical attachment strategies. The successful modification of MWNTs with semiconductor QDs has significant implications for materials research, and the door is now open for more extensive inquiries into the luminescent, electronic, and chemical properties of these unique building blocks as they are incorporated into new and functional multicomponent nanostructured materials.

Acknowledgments

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