

Quantum Dot Modified Multiwall Carbon Nanotubes

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A novel strategy for the fabrication of multiwall carbon nanotube–nanocrystal heterostructures is shown. Different quantum dots (QDs) with narrow size distributions were covalently coupled to carbon nanotubes (CNTs) and silica-coated CNTs in a simple, uniform, and controllable manner. The structural and optical properties of CNT/QD heterostructures are characterized by electron microscopy and photoluminescence spectroscopy. Complete quenching of the PL bands in both QD core and core/shell heterostructures was observed after adsorption to the CNTs, presumably through either carrier ionization or energy transfer. The deposition of a silica shell around the CNTs preserves the fluorescence properties by insulating the QD from the surface of the CNT.

Introduction

Metal/semiconductor heterostructures are believed to be useful building blocks for optoelectronic devices, solar energy converters, and photocatalysis.^{1–3} The physical and chemical properties of CNTs^{4–7} can be significantly altered through chemical surface modification, doping, and coating.^{8–12} The functionalization of the surface of CNTs with a variety of organic and inorganic species permits the fabrication of novel one-dimensional (1D) hybrid materials. To date, several types of semiconductor nanoparticles such as CdSe,^{13,14} CdSe@ZnS,^{15,16} CdS, and TiO₂¹³ have been covalently bound to the surface of CNTs. Previous reports on CNT/QD composites mostly employed oxidized CNTs, which arise from the treatment of CNTs with acids in order to form carboxyl functionalities (as well as keto, aldehyde, and alcoholic groups) on the nanotube surface. This oxidation leads to numerous side defects along the entire length of the CNTs, which disrupts the π -bonding symmetry of the sp² hybridized orbitals. As a consequence of the damage to the graphite lattice, the conductivity and other electrical as well as mechanical properties of the CNTs are strongly affected.^{13,15,17,18} As such, the utilization of carbon nanotubes for both electronic applications and charge-transfer investigations require a means to functionalize the surface of the CNTs in a way that does not compromise their electronic properties.

Recently, Chaudhary et al. showed a new approach for the conjugation of CdSe–ZnS core–shell nanocrystals (NC) to the surface of CNTs by electrostatic interaction between zinc ions and electronegative surfactants adsorbed on the oxidized CNTs.¹⁹ Carbon nanotubes were also used as templates for direct thermal growth of ZnO and ZnS,^{20,21} or in situ wet chemical synthesis of crystalline CdTe,²² CdS,²³ CdSe,²⁴ ZnS,^{25,26} TiO₂,²⁷ and CdS,²⁸ on the surface of the CNTs. However, nanocrystals that are directly grown on the surface of the carbon nanotubes exhibit large variations in shape and size in most cases. Since size-dependent optical and electrical properties of QDs meet a broad range of applications, homogeneity and narrow size distributions of nanocrystals are important for constructing optoelectronic devices with tailored properties.

Herein we report on a new class of multiwalled carbon nanotubes/quantum dots (MWNT/QD) heterostructures. Various colloidal semiconductor nanocrystals were covalently attached to MWNTs, which were pre-functionalized by a polymer wrapping technique that is not invasive and does not introduce defects to the structure of CNTs. A polyelectrolyte is simply adsorbed on the MWNTs surface but noncovalently bound. This method ensures high stability in a range of organic solvents. ZnO, CdSe, and CdSe–CdS nanoparticles with narrow size distributions were used in order to fabricate the composite MWNT/QD structures. Analogue experiments were carried out with MWNTs with an insulating silica shell. The MWNT@SiO₂ were produced using a previously reported method,²⁹ chemically modified, and subsequently coated with the desired QDs.

To our knowledge, only a few studies have been reported on the investigation of the photoluminescence of CNT/QD heterostructures.^{23,25} However, Du et al. showed MWNTs only partially coated with ZnS nanospheres of around 180 nm in diameter. Herein, we characterize quantum size semiconductor–metal and semiconductor–insulator–metal systems in terms of structural and optical properties.

Experimental Section

Materials. MWNTs (PECVD, purity >95%, diameter 10–20 nm, length 2–20 μ m) were obtained from NanoLab (Newton, MA). Poly(allylamin hydrochloride) (PAH), tetraethoxysilan (TEOS), ammonia solution (28–30%), and sodium chloride (NaCl) were purchased from Roth and used as obtained.

Preparation of ZnO Nanoparticles. We followed a previously reported technique for the preparation of ZnO nanocrystals.³⁰ Briefly, 4.39 g (0.02 mol) of zinc acetate dihydrate (Zn(Ac)₂·2H₂O) were dissolved in 31 mL of ethanol (EtOH) and refluxed for 45 min. Then 9 mL (0.02 mol) of tetramethylammonium hydroxide (TMAH) solution in methanol (25%) was added to the hot solution and stirred for several hours at room temperature. The resulting sol was washed by repeated centrifugation and redispersion in EtOH and was finally filtered through a 0.2 μ m pore membrane. Afterward, the solvent was removed in a rotary evaporator, resulting in a white powder, which can easily be redispersed in EtOH or chloroform. Such particles are 8–10 nm in the diameter.

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Preparation of CdSe Cores and CdSe/CdS Core–Shell Nanocrystals. The synthesis of the monodisperse CdSe cores was accomplished using the method of van Embden et al.³¹ The overcoating of these cores with both CdS and ZnS was undertaken using an adaptation of the SILAR technique (successive ion layer adsorption and reaction). In this way production of monodisperse NCs is possible in a broad range of sizes.

CNT Functionalization and Phase Transfer. The MWNTs were functionalized by polymer wrapping with (PAH). CNTs (50 mg) were dispersed in a 0.5 wt % PAH (Mw = 70000) salt solution (0.5 M NaCl, 500 mL), sonicated for 3 h, then stirred overnight at 80 °C, and again left in an ultrasonic bath for 2 h. Excess polymer was removed by repeated centrifugation and redispersion in water (five times), until a stable, homogeneous CNTs suspension was obtained. Amine functionalities on the MWNTs surface (MWNT-PAH) ensure good separation and stability due to electrostatic interactions (repulsions) in aqueous solution.

PAH modified carbon nanotubes can also be easily transferred to organic solvents. First, the aqueous dispersion of MWNTs is precipitated by centrifugation and redispersed in EtOH. After further centrifugation, the sediment may be redispersed into the desired organic solvent (e.g., chloroform, hexane) by short treatment in an ultrasonic bath. Carbon nanotubes–PAH suspensions in chloroform were found to remain stable for weeks.

Silica Coating. A simple and efficient method for silica coating of MWNTs was previously reported.²⁹ A MWNT-PAH water dispersion was added in a 5:1 volume ratio to a mixture of TEOS, H₂O, and ethanol (mass ratio 2:1:4). The mixture was sonicated and after 2 h set aside overnight at room temperature. After 12 h, the mixture was centrifuged to wash the carbon nanotubes with ethanol. The sediment was redispersed in a solution of ammonia in ethanol (4.2 vol % ammonia (28 wt % in water) in ethanol). Immediately after this, a TEOS solution (10 vol % in ethanol) was added under stirring (5 mL of TEOS in 500 mL ethanol solution of CNTs). The reaction mixture was stirred for another 8 h and sonicated from time to time. Finally, the CNTs were washed with ethanol and again redispersed. The process described above leads to the formation of a uniform and thick layer of silica on every individual MWNT. MWNT@SiO₂ structures form a stable suspension in EtOH and water. To modify the silica shell with amine functionalities, an ethanol solution of silica-coated CNTs was mixed and stirred with an appropriate amount of 3-aminopropyl trimethoxysilane (97%) (APS). In this reaction, silanization of APS occurs on the surface of silicon dioxide. The unreacted components were removed by washing with chloroform. This functionalization results in stable dispersions of MWNT@SiO₂ in organic as well as aqueous solutions.

Covalent Attachment of Semiconductor NPs to Functionalized MWNTs and MWNT@SiO₂. In a typical experiment, 15 μ L of 8 μ M solution of QDs was added to a 2 mL dispersion of functionalized MWNTs. The reaction mixture was briefly sonicated and then stirred for 15 min. Excess particles were removed by subsequent centrifugation and redispersion in chloroform. This procedure results in homogeneous coating of the MWNTs surface with nanocrystals.

An analogous approach was used for the connection of QD to multiwalled carbon nanotubes coated with a silica shell. MWNT@SiO₂ with amine functionalities were mixed with NPs. Through ligand exchange, the quantum dots were covalently attached to the amine moieties of the APS functionalized silica-

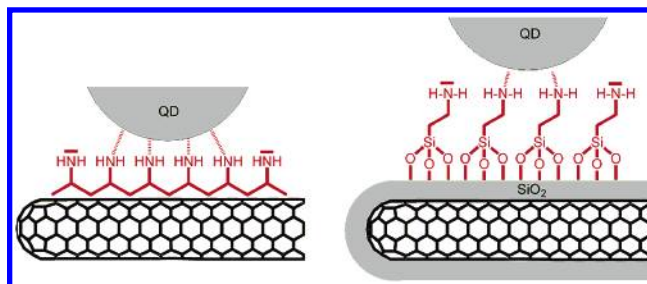


Figure 1. Schematic of the conjugation of QDs to MWNTs and MWNT@SiO₂.

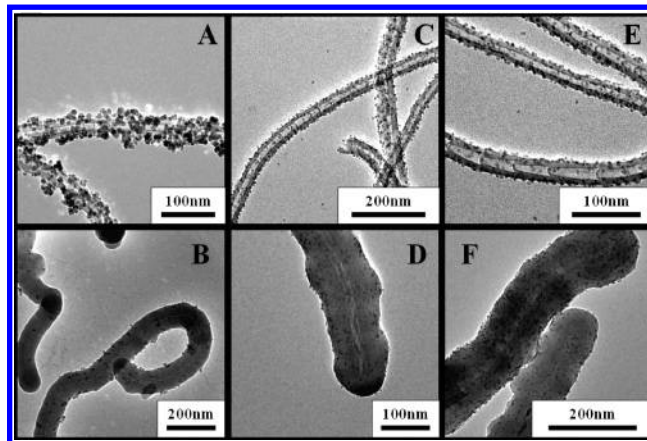


Figure 2. TEM images of hybrid materials from MWNT and MWNT@SiO₂ with ZnO (a, b), CdSe (c, d), and CdSe–CdS (e, f).

coated MWNTs. The final result is the uniform coating of QDs on the electrically insulated (SiO₂) surface of the MWNTs.

For UV–Vis absorption measurements in the range from 300 to 800 nm a Varian Cary 5000 spectrometer was used. Photoluminescence measurements are carried out on a Horiba Jobin Yvon FluoroMax-3 spectrometer.

Transmission electron microscopy was carried out on a Leo 922A with an acceleration voltage of 200 kV.

Results and Discussion

The schematic illustration shown in Figure 1 depicts the conjugation of both QDs to MWNTs and QDs to MWNT@SiO₂. The nanoparticles are covalently bound to amine functionalities that are present on the surface of MWNTs and silica-coated MWNTs. Direct evidence for the coupling of QDs to the functionalized carbon nanotubes is given by transmission electron microscopy. Figure 2 shows TEM images of quantum dots bound to the surface of MWNT and MWNT@SiO₂. In Figure 2a CNTs are covered with ZnO particles with an average diameter of about 10 nm. The same particles were used for decorating silica-coated MWNTs (Figure 2b). Figures 2c, 2d, 2e, and 2f display hybrid materials of MWNT/CdSe, MWNT@SiO₂/CdSe, MWNT/CdSe–CdS, and MWNT@SiO₂/CdSe–CdS, respectively.

The in situ chemical synthesis of semiconductor nanoparticles directly on the surface of carbon nanotubes usually leads to the formation of inhomogeneous crystalline structures with large polydispersity in shape and size.^{26,32,33} Our step-by-step process gives the flexibility to tailor the QDs prior to conjugation. Furthermore, the utilization of oxidized CNTs leads to nonuniform coverage of the surface as particles tend to be attached at the ends of carbon nanotubes and defect sides, where the concentration of carboxylic groups is the largest.^{13–15} The images in Figure 2 confirm that the QD nanoparticles are

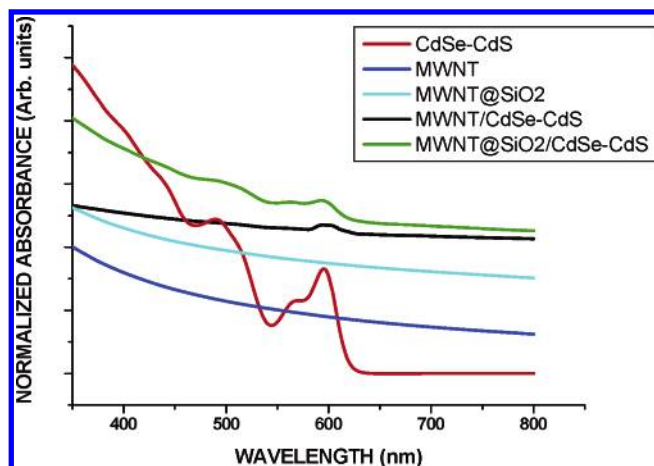


Figure 3. UV-Vis absorption spectrum of CdSe-CdS, MWNT, MWNT@SiO₂, MWNT/CdSe-CdS, and MWNT@SiO₂/CdSe-CdS.

homogeneous in size and shape, with even coatings along the entire lengths of the MWNTs. Notably, there are scarcely any unbound QDs with a few of the QDs making heterojunctions between individual carbon nanotubes.

In other reports on covalently conjugated QDs to CNTs, the procedure for the formation of these nanocomposites involves complex reactions and functionalizations, making these strategies more complicated and time-consuming.^{14–16,34} Our new strategy allows for straight coupling of QDs to CNTs from aqueous or organic dispersions of nanocrystals since the MWNT-PAH form stable dispersions in both polar and nonpolar solvents. This provides a further advantage as it allows for the investigation of these materials in media with a range of dielectric constants.

Figure 3 illustrates the UV-Vis absorption of MWNTs, and MWNT@SiO₂ before and after coupling reaction with CdSe-CdS quantum dots. The absorption spectrum of the CdSe-CdS QDs is also shown for reference. As expected, the MWNTs and MWNT@SiO₂ give featureless absorption spectra, with a higher degree of scattering in the MWNT@SiO₂ sample arising from the silica shell. Due to the light scattering of MWNTs and silica, and the low concentration of NCs, the characteristic UV-Vis signal of QDs cannot fully be resolved. Even so, the spectra of MWNT@SiO₂/QD and MWNT/QD do exhibit weak features directly corresponding to the absorption edge of CdSe-CdS QDs. This is consistent with other reports, in which is shown that UV-Vis spectra of CNT/QD systems do not display any extra features that would arise from charge diffusion or electronic interaction between the CNTs and QDs in their ground state.^{14,26,28} Only selected spectra obtained from nanocomposites containing CdSe-CdS quantum dots are shown in Figure 3. Despite this, consistent results were achieved for all CNT/QD heterostructures fabricated in this study (specifically MWNTs and MWNT@SiO₂ with ZnO, CdSe).

Recently, it has been reported that carbon nanotubes can act as electron acceptors in their photoexcited state, wherein charge and energy transfer between conjugated species and CNTs may occur.^{3,35–38} Given the work function of MWNTs is estimated to be of 4.4–5.1 eV^{39,40} and the Fermi level lies in the HOMO-LUMO gap of the CdSe nanoparticles, MWNTs are capable of efficient electron scavenging (refer to Figure 5). Figure 4a represents PL spectra of CdSe (red line), MWNT/CdSe (blue line), MWNTs (green line), and MWNT@SiO₂/CdSe (black line). The characteristic luminescence peak for CdSe particles with an average size of 4.2 nm is located at 591 nm. It is observed that the PL band from the QDs disappears after

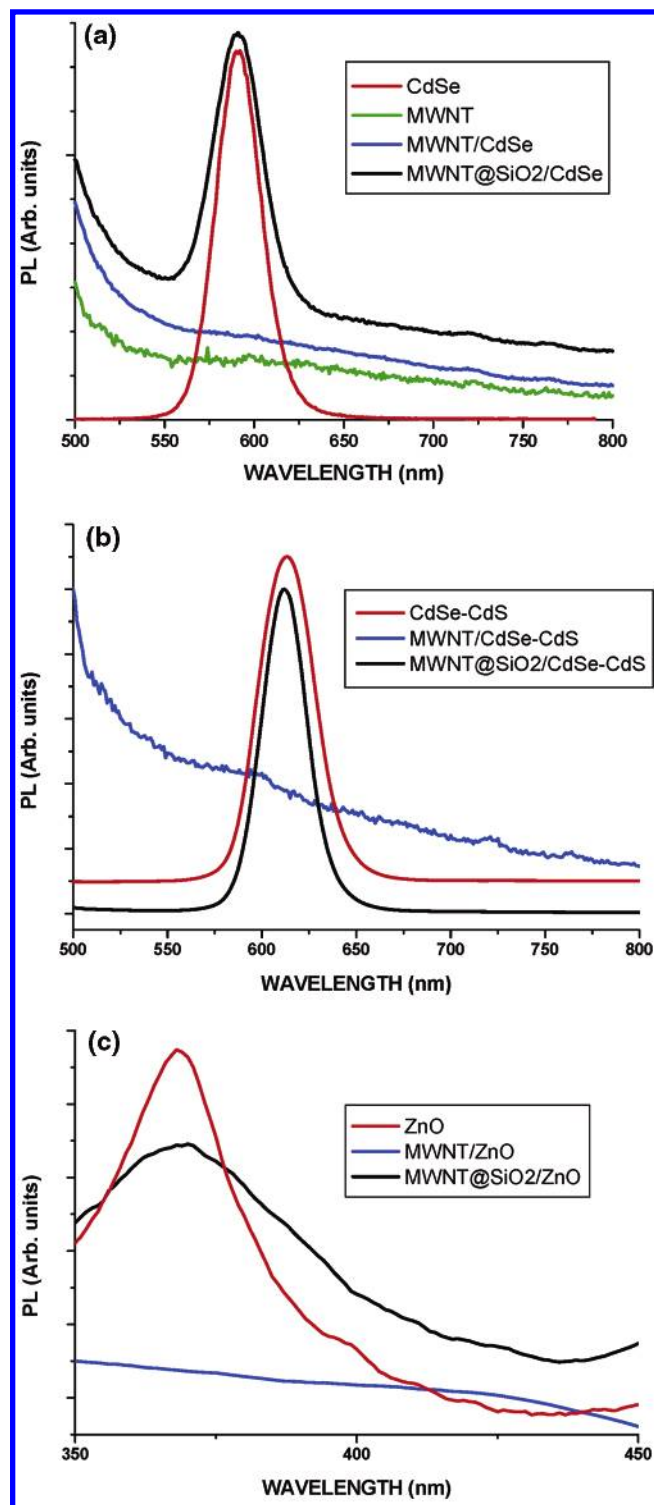


Figure 4. PL spectra of CNT/QD and CNT@SiO₂/QD heterostructures: (a) CdSe (red line), MWNT/CdSe (blue line), and MWNT@SiO₂/CdSe (black line) $\lambda_{\text{ex}} = 440$ nm; (b) CdSe-CdS (red line), MWNT/CdSe-CdS (blue line), and MWNT@SiO₂/CdSe-CdS (black line), $\lambda_{\text{ex}} = 440$ nm; (c) ZnO (red line), MWNT/ZnO (blue line), and MWNT@SiO₂/ZnO (black line), $\lambda_{\text{ex}} = 300$ nm.

conjugation to MWNT. There are three possible explanations for this quenching: hole transfer, electron transfer, or both into the MWNTs. We hypothesize that interactions between MWNTs and QDs involve charge transfer of photoexcited electrons from the conductive band of the donor (QDs) to the empty electronic states of the acceptor (MWNTs), resulting in nonradiative decay of the QD excited state (Figure 5).

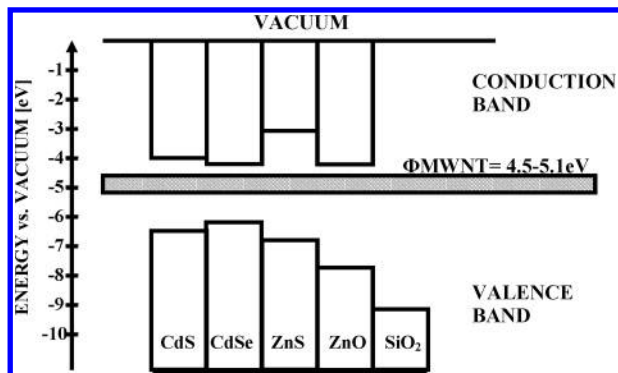


Figure 5. Schematic energetic band positions for MWNT, SiO₂, CdSe, CdSe–CdS, CdSe–ZnS, and ZnO.^{43,44}

In contrast, the PL spectrum of MWNT@SiO₂/CdSe nanocomposites still displays the QD emission peak at 591 nm. As we used similar concentrations of MWNT and MWNT@SiO₂ with the same amount of CdSe nanocrystals in each sample, the results shown in Figure 4a clearly demonstrate that the quenching of the QDs emission is suppressed by overcoating the MWNT with silica. The large band gap and thickness of the SiO₂ layer rule out both charge transfer and electron tunneling as possible quenching mechanisms, further supporting our supposition that quenching is a result of electron injection into the MWNT. Moreover, the observed quenching does not relate to interactions of QD with ligand functionalities that covalently link the QDs to the MWNTs as APS was used as the coupling agent in both cases. Second, amine ligands are commonly used for passivation of surface defects (electron traps) of CdSe nanocrystals and do not introduce trapping energy levels into the band gap of these quantum dots.³¹

In principle, the overcoating of one semiconductor with another of a wider band gap should completely confine the charge carriers to the core. Interestingly, luminescence quenching is also observed from the CdS overcoated particles (Figure 4b). However, the conduction band offsets between CdSe and CdS are small (~ 0.32 eV), and as such the lighter, more mobile electron may tunnel through the shell.⁴¹ Given that MWNTs are appropriate acceptors, the electron may be scavenged by the MWNT, resulting in nonradiative decay or even permanent oxidation. Furthermore, the lattice mismatch between CdSe and CdS, although relatively small ($\sim 3.9\%$), will inevitably result in dislocations and other defects, which will aid carrier diffusion from the core to the surface of the QD.⁴² Overcoating the MWNTs with silica is again seen to prevent quenching.

The CNT/ZnO structures exhibit corresponding optical properties as observed for MWNT/CdSe–CdS composites. Figure 4c shows the PL spectra of ZnO (red line), MWNT/ZnO (blue line), and MWNT@SiO₂/ZnO (black line). As expected, the luminescence quenching is observed for the MWNT/ZnO hybrid material and the silica shell over the carbon nanotubes successfully blocks the charge transfer between QDs and MWNTs. The photoluminescence peak of MWNT@SiO₂/ZnO is broadened compared to the PL peak of pure ZnO, most likely due to the aggregation of ZnO on the silica surface.

Conclusions

In summary, a new approach is shown for the preparation of MWNT/NCs heterostructures with a highly defined morphology. QDs on bare MWNT were found to exhibit no luminescence, while the MWNT@SiO₂/QD composites retained their luminescence. The ability to allow or prevent charge transfer from photoexcited QDs to CNT opens up promising possibilities for

applications in photoelectric and optical devices, biological sensors, and catalytic materials.

Note Added after ASAP Publication. This article was published ASAP on June 2, 2006. Two author names were removed at their request. Also, an additional citation was added to ref 15. The correct version was reposted on June 13, 2006.

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