

Quantum Dot Modified Multiwall Carbon Nanotubes

Maciej Olek*, Thomas Büsgen*, Joel van Embden**, Michael Hilgendorff*, Paul Mulvaney**, and Michael Giersig*

* Center of Advanced European Studies and Research (caesar), Bonn, Germany
olek@caesar.de

** University of Melbourne, Australia

ABSTRACT

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.

Keywords: carbon nanotubes, quantum dots, nanocomposites, photoluminescence, quenching.

1 INTRODUCTION

Metal/Semiconductor heterostructures are believed to be useful building blocks for optoelectronic devices, solar energy converters, and photocatalysis [1]. The physical and chemical properties of CNTs can be significantly altered through chemical surface modification, doping, and coating [2]. 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. 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 sp^2 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 [3, 4]. 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.

Carbon nanotubes were also used as templates for direct thermal growth of ZnO and ZnS [5], or *in-situ* wet

chemical synthesis of crystalline quantum dots [6, 7] on the surface of the CNTs. However, such nanocrystals exhibit large variations in shape and size in most cases.

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 MWNT's surface but non-covalently 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 [8], chemically modified, and subsequently coated with the desired QDs.

Herein, we characterize quantum size semiconductor-metal and semiconductor-insulator-metal systems in terms of structural and optical properties.

2 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 %), 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 [9].

Preparation of CdSe cores and CdSe/CdS core-shell nanocrystals: The synthesis of the CdSe cores was accomplished using the method of van Embden *et al* [10]. 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).

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) and 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

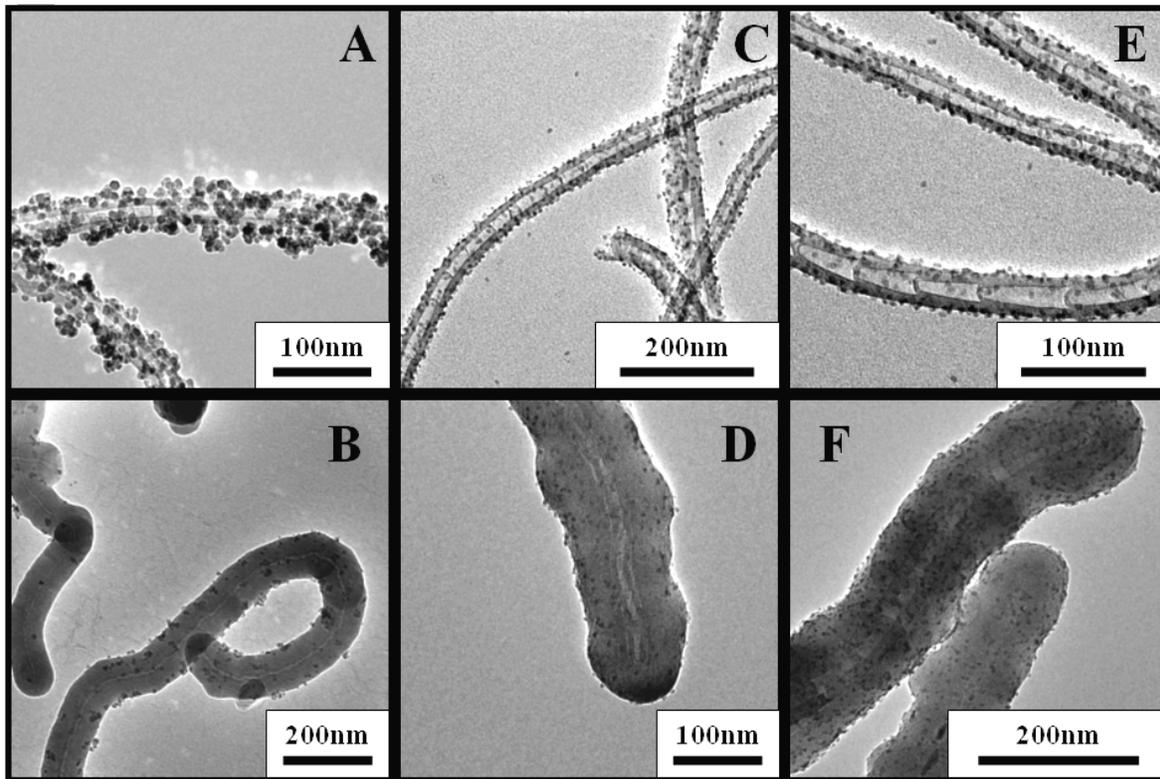


Fig. 1 TEM images of hybrid materials from: MWNT and MWNT@SiO₂ with ZnO (a, b), CdSe (c, d), and CdSe-CdS (e, f)

water (five times), until a stable, homogenous 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. Firstly, 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 [8]. MWNT@SiO₂ structures form a stable suspension in EtOH and water. In order 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 in aqueous solutions.

Covalent attachment of semiconductor NPs to functionalized MWNTs and MWNT@SiO₂. In a typical experiment, an appropriate amount of QDs was added to a chloroform dispersion of functionalized MWNTs. The reaction mixture 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 MWNT's 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 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 by a Horiba Jobin Yvon FluoroMax-3 spectrometer. Transmission electron microscopy was carried out on a Leo 922A with an acceleration voltage of 200 kV.

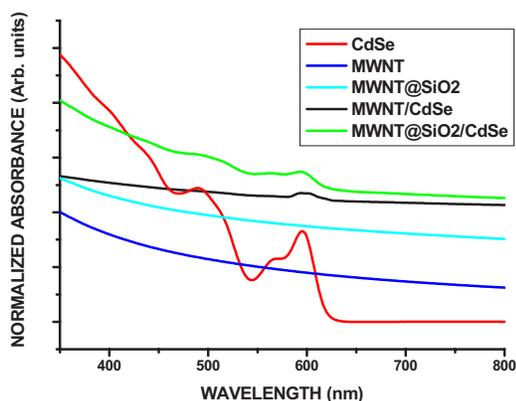


Fig. 2 UV-Vis absorption spectrum of CdSe-CdS, MWNT, MWNT@SiO₂, MWNT/CdSe-CdS, and MWNT@SiO₂/CdSe-CdS.

3 RESULTS AND DISCUSSION

Direct evidence for the coupling of QDs to the functionalized carbon nanotubes is given by transmission electron microscopy. Figure 1 shows TEM images of quantum dots bound to the surface of MWNT and MWNT@SiO₂.

The *in-situ* chemical synthesis of semiconductor nanoparticles directly on the surface of carbon nanotubes, usually leads to formation of inhomogeneous crystalline structures with large polydispersity in shape and size [11]. Our step-by-step process gives the flexibility to tailor the QDs prior to conjugation. Furthermore, the utilization of oxidized CNTs leads to non-uniform 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 [4]. The images in Figures 1 confirm that the QD nanoparticles are 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.

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 non-polar solvents. This provides a further advantage as it allows for the investigation of these materials in media with a range of dielectric constants.

Figure 2 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

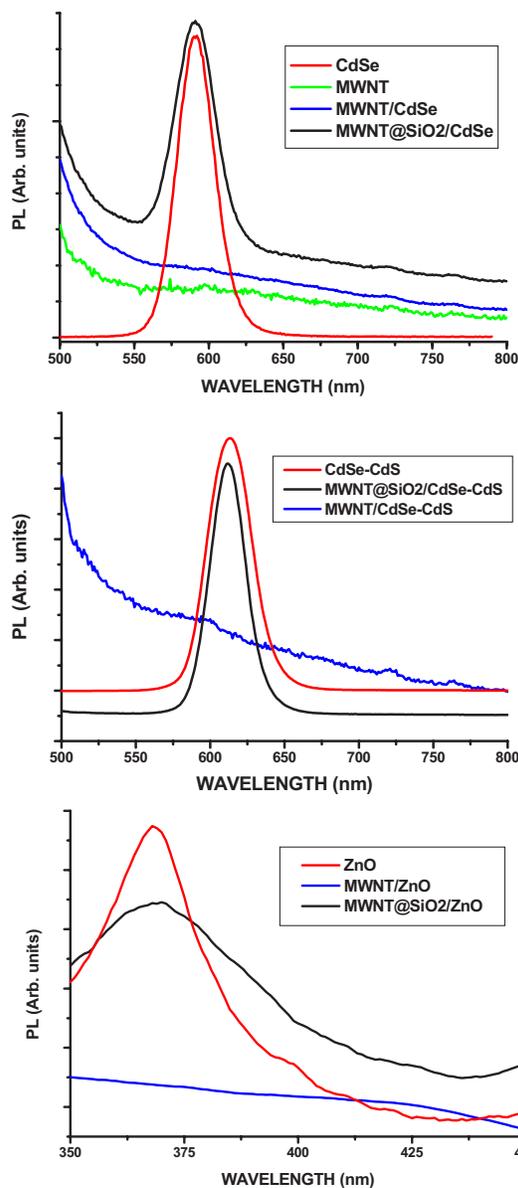


Fig. 3 PL spectra of CNT/QD and CNT@SiO₂/QD heterostructures: a) CdSe (red line), MWNT/CdSe (blue line) and MWNT@SiO₂/CdSe (black line), $\lambda_{\text{ex}} = 440$ nm; b) CdSe-CdS (red line), MWNT/CdSe-CdS (blue line) and MWNT@SiO₂/CdSe-CdS (black line), $\lambda_{\text{ex}} = 440$ nm; c) ZnO (red line), MWNT/ZnO (blue line) and MWNT@SiO₂/ZnO (black line), $\lambda_{\text{ex}} = 300$ nm.

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 [12]. Consistent results were achieved for all CNT/QD heterostructures fabricated in this study (specifically MWNTs and MWNT@SiO₂ with ZnO, CdSe).

Figure 3a 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 591nm. It is observed that the PL band from the QDs disappears after 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 non-radiative decay of the QD excited state.

In contrast, the PL spectrum of MWNT@SiO₂/CdSe nanocomposites still displays the QD emission peak at 591nm. As we used similar concentrations of MWNT and MWNT@SiO₂ with the same amount of CdSe nanocrystals in each sample, the results shown in Fig. 3a 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. Secondly, 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 [10].

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 3b). 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 [13]. Given that MWNTs are appropriate acceptors, the electron may be scavenged by the MWNT resulting in non-radiative decay or even permanent oxidation. Furthermore, the lattice mismatch between CdSe and CdS, although relatively small (~3.9 %), will inevitably result in dislocations and other defects, which will aid carrier diffusion from the core to the surface of the QD [14]. 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 3c shows the PL spectra of ZnO (red line), MWNT/ZnO (blue line) and MWNT@SiO₂ (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.

4 CONCLUSIONS

In summary, 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 photo-excited QD's to CNT opens up promising possibilities for applications in photoelectric and optical devices, biological sensors and catalytic materials.

REFERENCES

- [1]. Subramanian V, Wolf EE, Kamat PV. *Journal of the American Chemical Society* 2004; 126(15):4943-50.
- [2]. Balasubramanian K, Burghard M. *Small* 2005;1(2):180-92.
- [3]. Ravindran S, Chaudhary S, Colburn B, Ozkan M, Ozkan CS. *Nano Letters* 2003;3(4):447-53.
- [4]. Banerjee S, Wong SS. *Nano Letters* 2002; 2(3):195-200.
- [5]. Kim H, Sigmund W. *Journal of Crystal Growth* 2003; 255 (1-2):114-8.
- [6]. Banerjee S, Wong SS. *Advanced Materials* 2004; 16(1):34.
- [7]. Banerjee S, Wong SS. *Chemical Communications* 2004; (16):1866-7.
- [8]. Olek M, Kempa K, Jurga S, Giersig M. *Langmuir* 2005; 21(7):3146-52.
- [9]. Hilgendorff M, Spanhel L, Rothenhausler C, Muller G. *Journal of the Electrochemical Society* 1998; 145(10):3632.
- [10]. van Embden J, Mulvaney P. *Langmuir* 2005; 21(22):10226-33.
- [11]. Banerjee S, Wong SS. *Journal of the American Chemical Society* 2003; 125(34):10342-50.
- [12]. Haremza JM, Hahn MA, Krauss TD. *Nano Letters* 2002; 2(11):1253-8.
- [13]. Xie RG, Kolb U, Li JX, Basche T, Mews A. *Journal of the American Chemical Society* 2005;127(20):7480-8.
- [14]. Li JB, Wang LW. *Applied Physics Letters* 2004; 84(18):3648-50.