

## **Heterojunctions of Multi-Walled Carbon Nanotubes and Semiconducting Nanocrystals for Electronic Device Applications**

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### **Abstract**

Conventional device fabrication strategies must be augmented by new techniques including self assembly methods in order to truly take advantage of the quantum nature of novel nanoscale electronic devices and systems and permit the use of these properties for "real" applications in a larger system ( $> 10$  nm and  $< 1$   $\mu$ m). In this talk, I will describe a novel technique for the fabrication of nano-assemblies of carbon nanotubes (CNT) and quantum dots (QD) -formation of CNT-QD conjugates-. Heterojunctions of QD's and MWCNT's could become better alternatives for the synthesis of nanoscale devices which would preserve the electronic properties of MWCNT's compared to configurations that depend on the bending or overlapping of CNT's. Such configurations could be useful for the bottom-up assembly of nanoscale circuits or as drop-in technologies for the existing device platforms. During processing, CNT's are primarily functionalized with carboxylic end groups by oxidation in concentrated sulfuric acid. Thiol stabilized QD's in aqueous solution with amino end groups were conjugated to carbon nanotubes using the ethylene carbodiimide coupling reaction. Detailed chemical and physical characterization of the heterojunctions have been conducted using Fourier transform infrared spectroscopy, transmission electron microscopy and energy dispersive spectroscopy.

### **Introduction**

1-D nanostructures have considerable potential as building blocks in future electronics. The unique electrical, mechanical, and chemical properties of carbon nanotubes have made them intensively studied materials in the field of nanotechnology<sup>1-4</sup>. A number of device applications of these nanoscale materials have been envisioned<sup>5-10</sup>. Single-walled carbon nanotubes (SWCNTs)<sup>11</sup> and multi-walled carbon nanotubes (MWCNTs)<sup>12,13</sup> under special conditions have been shown to possess ballistic conduction behavior, which makes them attractive candidates for field emission devices<sup>14</sup>. SWCNTs indicate either metallic or semiconductor behavior depending on their chirality<sup>15</sup> and radial dimension<sup>16,17</sup>. Although the electronic properties of MWCNTs<sup>18-20</sup> are less well known, they have been shown to exhibit either metallic<sup>19</sup> or semiconducting properties<sup>20</sup> depending on their outermost shell. The inter-shell interactions in a MWCNT are weak, therefore, electrical transport is confined to the outermost shell<sup>17</sup>. It has been shown recently that it is possible to manipulate the electrical properties of a MWCNT by using current induced oxidation to systematically breakdown the outermost shells layer by layer<sup>21</sup>. This opens up the possibility of selecting the tube with the desired electrical property. In addition, doping<sup>8</sup> and introduction of defects<sup>20</sup> or distortion<sup>22</sup> in the CNTs have also been utilized for manipulating their energy band structure. The versatile electrical properties of CNTs make them promising candidates for nanoscale electronic devices<sup>12,14,23,24</sup>, especially transistors<sup>25,26</sup>. In most of the previous work on CNT based nanoscale transistors, the control over the electrical properties of the devices have been limited. In addition, these devices relied on overlapping CNTs<sup>26</sup> for forming junctions, which introduces local bending. Experiments carried out to study the electromechanical properties<sup>22</sup> of carbon nanotubes indicated that the distortion of a CNT resulted in a decrease in its conductivity. Dai reported in their simulations<sup>4</sup> that such distortions due to

bending leads to an electron transport barrier and is mainly responsible for the reduced electrical conductance of the nanotube system.

Alternatively, semiconducting nanomaterials can be conjugated with carbon nanotubes to create heterojunctions which could be useful for the fabrication of novel devices. Quantum dots (QDs)<sup>27</sup>, which are semiconducting nanocrystals, possess size tunable electronic and optical properties resulting from quantum confinement<sup>28</sup>. They offer high resistance to photo bleaching thus making them attractive materials for optoelectronics<sup>29,30</sup> and in-vivo biosensing applications<sup>31</sup>. The development of carbon nanotube–quantum dot heterojunctions have recently received interest resulting from developments in chemical modification of CNTs.



**Figure 1.** Schematic of the conjugation of MWCNTs to ZnS capped CdSe nanocrystals. (A) As grown MWCNTs (I) were oxidized by refluxing it in HNO<sub>3</sub> at 130 °C for 24 h to open the ends and create carboxylic group terminating MWCNTs (II). (B) ZnS capped CdSe QDs in chloroform (III) agitated with AET to stabilize them in aqueous PBS (IV). (C) Heterojunctions of CNT-QDs were synthesized by using a zero length cross linker EDC.

In this paper, we report the synthesis of heterojunctions with controlled conjugation of water stabilized, amine terminating, ZnS coated CdSe QDs (QD-NH<sub>2</sub>) to acid treated ends of MWCNTs. Figure 1 illustrates the procedure used in the synthesis of the heterojunctions. Recently, fluorescent imaging of carbon nanotubes<sup>32,33</sup> has been reported. The drawback of a covalent attachment of a fluorescent molecule to a CNT is the quick decay of lifetime and the low quantum yield of the fluorescent label. This problem can be overcome by using quantum dots, which are superior substitutes for organic fluorescent molecules. Otake et al. reported the fluorescence visualization of CNTs<sup>33</sup> by modifying them with silicon-based polymers in order to observe real time fluidic behavior during electrophoresis<sup>34</sup>. They observed entangled cotton like fluorescent fibers of nanotubes. Our heterostructures with quantum dots not only have high quantum yield and long life but also are well dispersed individual units that facilitate monitoring real time fluidic behavior and fluorescent imaging in biosystems.

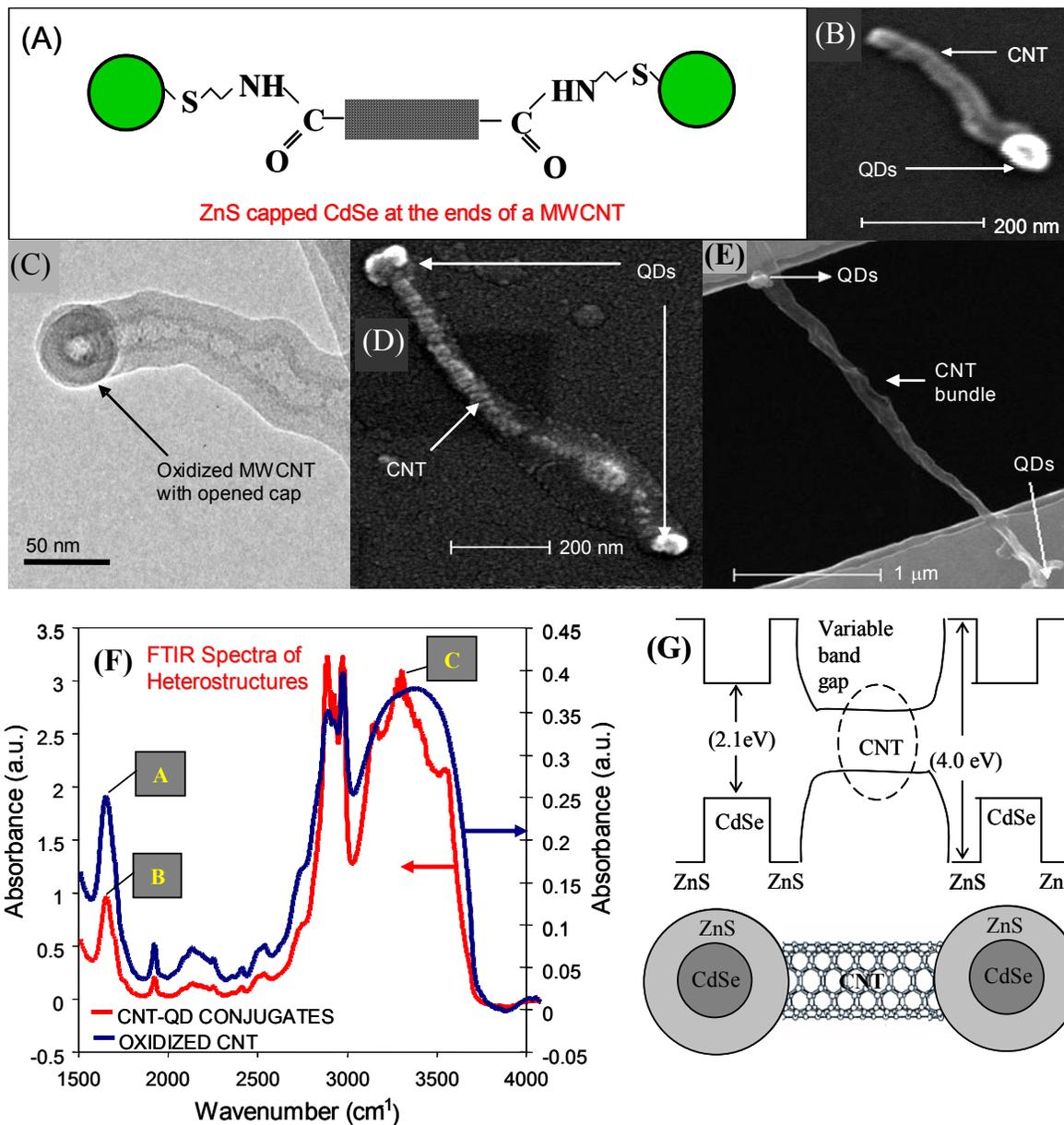
## **Experimental Procedures**

As grown MWCNTs (Nanostructured & Amorphous materials, Inc., Los Alamos) were oxidized by refluxing at 130 °C in nitric acid for 24 hours. It has been reported that multi walled CNTs get oxidized at a slower rate compared to single walled CNTs<sup>35</sup>. The use of Nitric acid reflux oxidizes MWCNTs mildly and preferentially at their ends. This changes the character at the ends of the CNTs from hydrophobic to hydrophilic. The acid treated CNTs were washed with distilled water several times and finally vacuum filtered using a 0.1 μm polycarbonate filter. The filtered CNT cake was dried by heating at 150 °C for 24 hours. The acid treatment, apart from introducing acid groups at the end of the CNT, oxidizes the graphitic impurities present along with the CNTs. After oxidation, the CNTs are shorter and are left with the carboxylic groups that impart a hydrophilic nature and facilitate further functionalization. ZnS capped CdSe QDs (Evident Technologies, Inc., New Jersey) were used in the functionalization of the MWCNTs. ZnS coating over the CdSe core improves the quantum yield by passivating the surface dangling bonds (carrier trap sites) and also eliminates the toxic nature of the CdSe core, enabling them for use in biosystems. To prepare water stabilized QDs (QD-NH<sub>2</sub>), ZnS capped CdSe nanocrystals were suspended in chloroform by sonication for 30 minutes. Equal volumes of 1.0 M 2-aminoethane thiol hydrochloride (AET) were added to this QD solution. This resulted in a two-phase mixture with the aqueous aminoethane thiol forming an immiscible layer above the organic chloroform-QD suspension. The mixture was stirred vigorously on a magnetic plate for 4 hours after which it was allowed to settle down for a few minutes. Phosphate buffer saline (PBS, pH=7.5) was added to the solution at a 1:1 volume ratio. This was then mixed again in a vortex mixer for an hour. The water stabilized QDs are separated from AET by centrifuging it and re-suspending them in PBS a couple of times. When ZnS capped CdSe QDs were reacted with AET, the mercapto group in the thiol bonded to the Zn atoms and the amine groups rendered the QDs hydrophilic. The aqueous phase containing the QD-NH<sub>2</sub> was extracted for use in the EDC reaction. To form the CNT-QD heterostructures, we followed a two step coupling procedure using 1-Ethyl-3-(3-Dimethylaminopropyl) Carbodiimide HCl (EDC, Pierce Chemicals, Inc.) in the presence of N-Hydroxysuccinimide (sulfo-NHS, Pierce Chemicals, Inc.), and the reaction was carried out in PBS. The EDC reagent activates the terminal carboxylic groups of the CNTs forming a highly reactive o-acylisourea intermediate, which undergoes a rapid hydrolysis to re-form the acid. However, in the presence of sulfo-NHS, a more water soluble sulfo-succinimidyl intermediate is formed. This intermediate readily undergoes nucleophilic substitution with primary amines on the QD surface forming amide linkages. The EDC reaction was carried out for 8 hrs at 50 °C under continuous mixing.

## **Results and Discussion**

Characterization of the heterostructures was conducted using scanning electron microscopy, transmission electron microscopy and Fourier transform infrared spectroscopy. A drop of the reaction mixture containing the CNT-QD complexes is placed on a silicon chip and dried in a vacuum desiccator for preparing the SEM samples. Holey carbon coated copper grids were used for preparing the TEM samples. Figure 2(b) and 2(d) are SEM images of the CNT-QD conjugates. The rough appearance of the MWCNT in Figure 2(d) is due to excess gold sputtering resulted during SEM sample preparation. We observe that sidewall functionalizations are absent because of the mild oxidation conditions imposed which only removes the cap region (Figure 2(c)). The length of the MWCNTs in these figures are between 400-1000 nm. The ends of the oxidized MWCNTs produce multiple carboxylic groups depending on the number of concentric nanotubes and their diameter at their ends which results in the

conjugation of multiple QDs at the end regions. The size of these QD clusters are ideal for providing electrical contacts when used for device applications.



**Figure 2.** (a) The bonding of MWCNT and nanocrystals is illustrated. (b) SEM image of a MWCNT end-conjugated to a QD cluster. No sidewall functionalization is present. (c) TEM image of an oxidized MWCNT with cap removed. (d) SEM image of a MWCNT-QD-MWCNT heterostructure. No sidewall functionalizations present. (e) A heterostructure electrostatically assembled over parallel interconnects for measurements. (f) FTIR spectra for oxidized MWCNT and MWCNT-QD heterostructures. (g) Band diagram for the MWCNT-QD-MWCNT heterostructure is illustrated.

Our conjugations are so specific even for MWCNTs as long as several μm), the QDs are observed only at the CNT ends. This indicates the highly selective end functionalization

of the CNTs with our process. As indicated by Haremza et al.<sup>30</sup>, sidewall functionalization is acceptable for some applications such as chemical and biosensing in addition to fabrication of composites; but for electronic devices, side wall functionalization disrupts the  $\pi$ -bonding symmetry of the  $sp^2$  hybridization and compromises the unique electronic properties of the CNTs. For successful device applications, the CNT electronic structure should remain unaffected, and this can be achieved only by preferential oxidation of the CNT tips. Figure 2(f) shows FTIR spectra obtained for oxidized MWCNT's and for the MWCNT-QD heterostructures. Peaks A and B indicate the C=O stretch for the carboxylic groups for plain and a reduction in the peak amplitude (peak B) and a shift in the peak position indicated that the acid groups have been utilized for the conjugation via amide bond formation. In addition, the appearance of peak C indicating the presence of N-H stretching peak corresponding to amide bond confirms the formation of covalent bonding during heterostructure formation. Current research involves the electrical characterization of heterojunctions such as the one shown in Figure 2(e), and the aligned bandstructure is depicted in Figure 2(g). We have done some initial experiments to align these heterojunctions across  $2\mu\text{m}$  wide and  $2\mu\text{m}$  thick aluminum serpentine structures over a Si/SiO<sub>2</sub> substrate. When acid treated CNTs suspended in distilled water are dispersed on a silicon substrate containing the hydrophilic aluminum interconnects (due to the thin native oxide layer), the hydrophilic ends of the carbon nanotubes self assemble themselves. Figure 2(e) shows an SEM images of a MWCNT bundle conjugated with QDs at the ends across the metal lines. Electrical characterization of these heterojunctions will be reported in a future publication. The current phase in our research is aimed at developing strategies for the three dimensional hierarchical self assembly of nanostructures.

### Conclusion

We have reported a method to synthesize heterojunctions of individual MWCNTs with QDs preferentially at the MWCNT ends. Due to the mild and well-controlled oxidation of the MWCNTs, conjugation occurs only at the ends for CNTs. The controlled conjugation process is very important in preserving the electronic properties of the CNTs and enabling the nanoassembly of electronic devices. Heterojunctions developed are water stabilized and thus can be further functionalized easily, which can be used as building blocks for various nanoscale electronic or optoelectronic devices and hierarchical assembly of multilayered systems.

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