

Supporting Information for

“Probing Differential Optical and Coverage Behavior in Nanotube-Nanocrystal Heterostructures Synthesized by Covalent versus Non-covalent Approaches”

Lei Wang¹, Jinkyu Han², Jessica Hoy^{2,4}, Fang Hu³, Haiqing Liu¹, Molly M. Gentleman³,

Matthew Y. Sfeir⁴, James A. Misewich², and Stanislaus S. Wong^{1,2,*}

Email: sswong@bnl.gov; stanislaus.wong@stonybrook.edu

¹Department of Chemistry, State University of New York at Stony Brook,

Stony Brook, NY 11794-3400

²Condensed Matter Physics and Materials Sciences Department, Brookhaven National

Laboratory, Building 480, Upton, NY 11973

³Materials Sciences Department, State University of New York at Stony Brook,

Stony Brook, NY 11794-2275

⁴Center for Functional Nanomaterials, Brookhaven National Laboratory,

Building 735, Upton, NY 11973

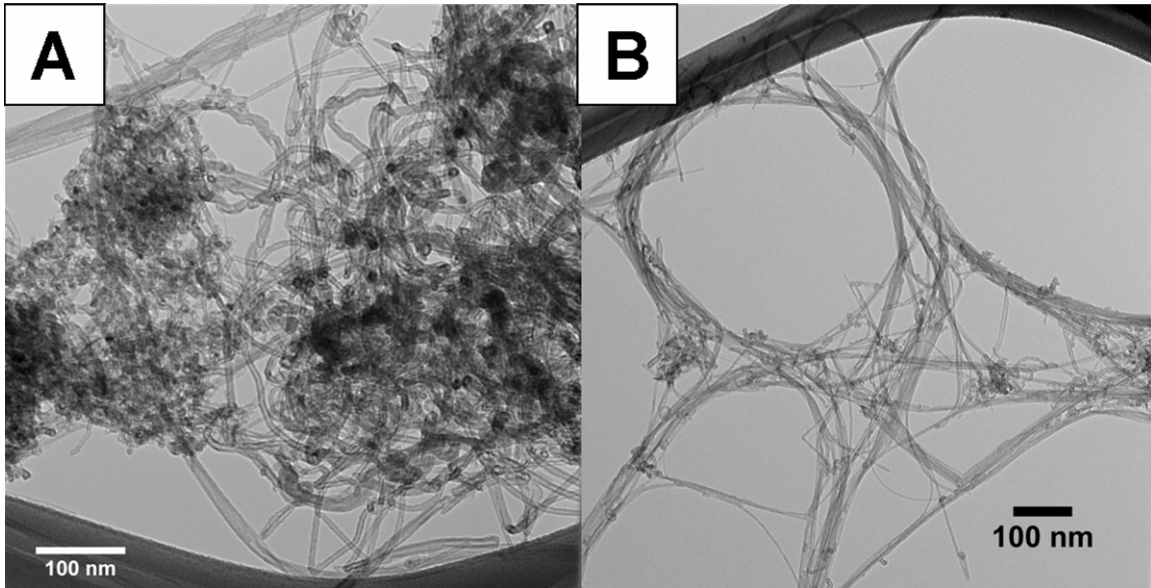


Figure S1. TEM images of (A) pristine and (B) purified DWNTs.

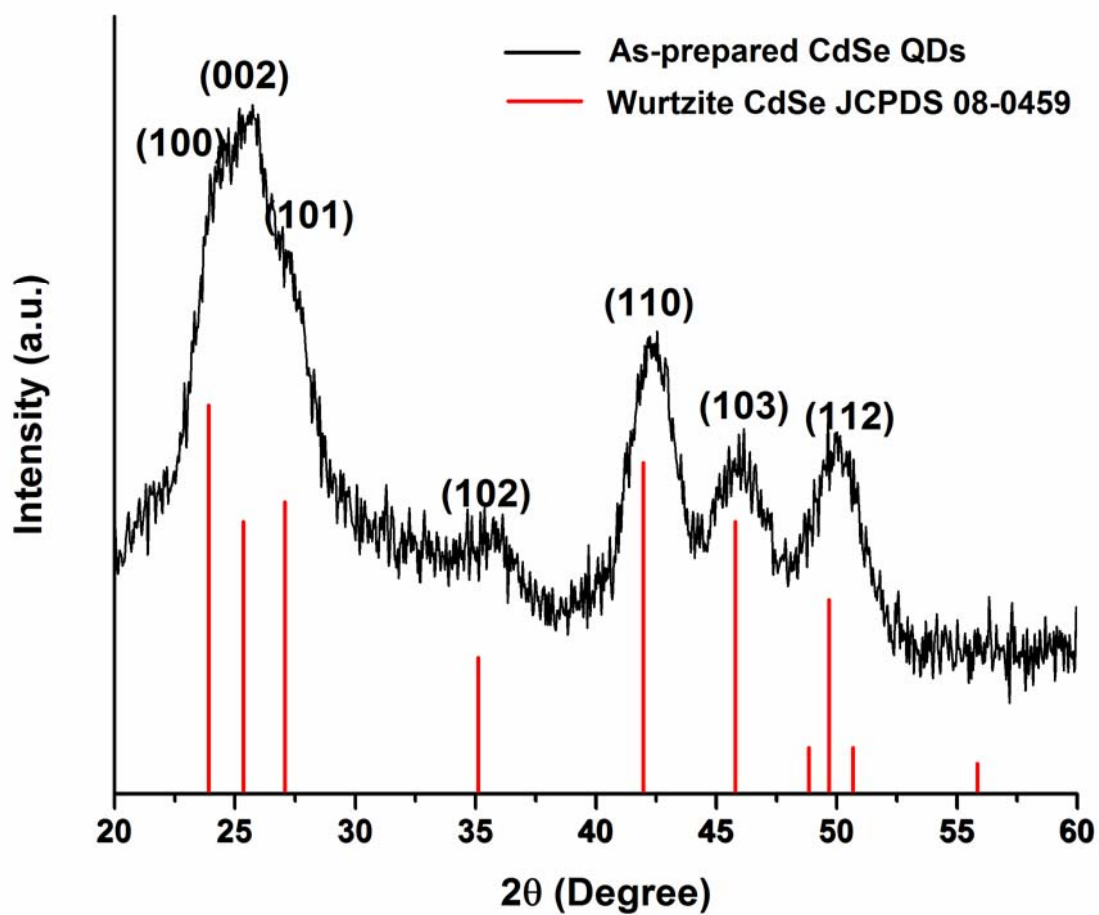


Figure S2. XRD of as-prepared CdSe QDs. Corresponding literature database standard (JCPDS #08-0459) is shown immediately below and highlighted in red.

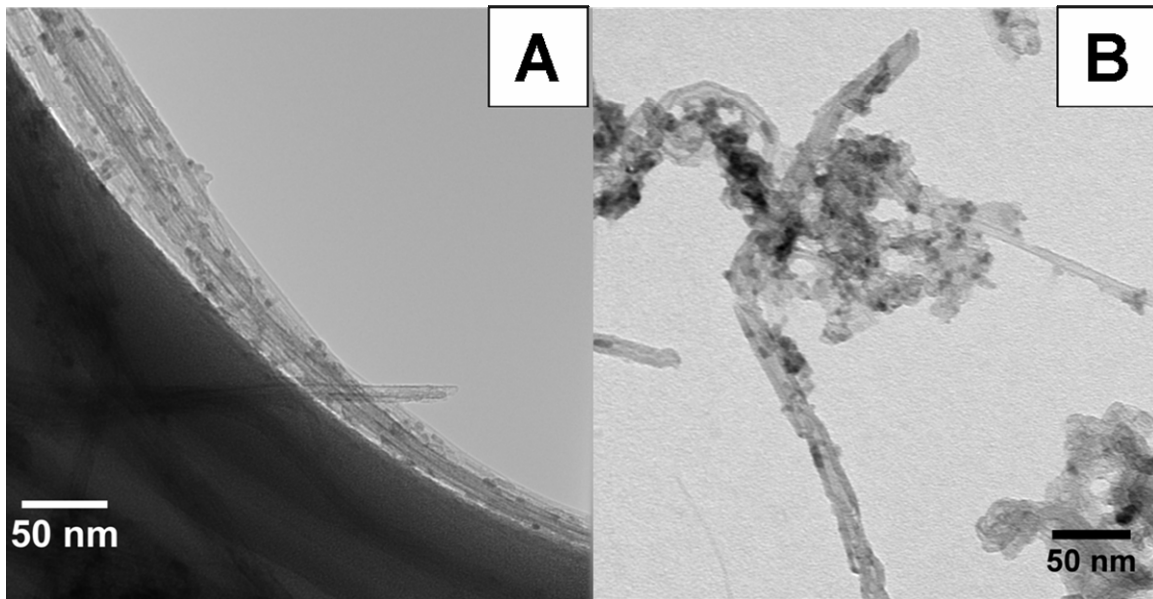


Figure S3. TEM images of DWNT-4-ATP-CdSe heterostructures synthesized by a covalent attachment protocol, mediated using (A) DCC and (B) EDC linkers as coupling agents, respectively.

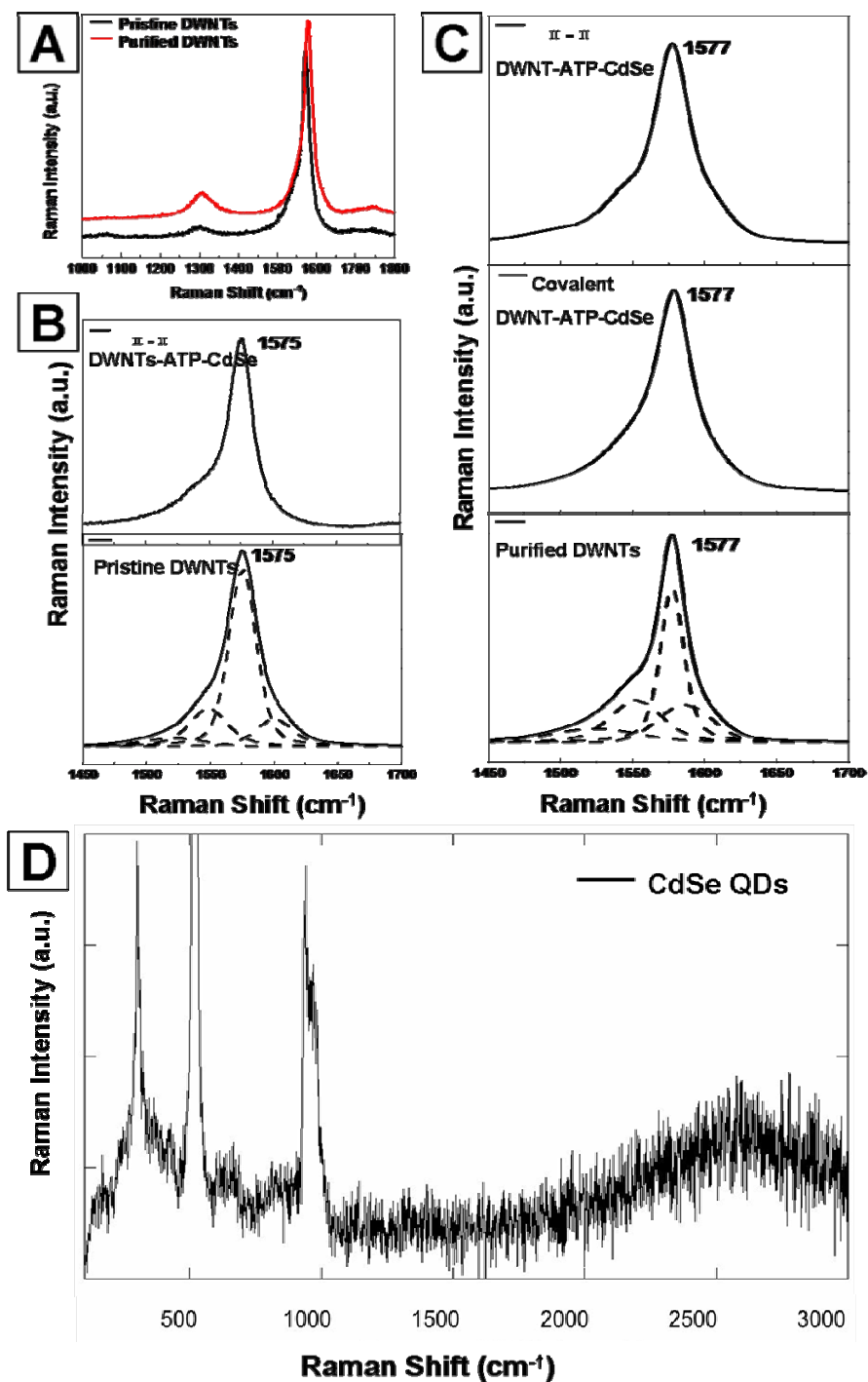


Figure S4. Raman spectra measured at an excitation wavelength of 785 nm (1.58 eV) of (A) pristine and purified DWNTs, (B) G band analysis of pristine DWNT as well as pristine DWNT-4-ATP-CdSe heterostructures, generated by non-covalent π - π stacking, (C) G-band analysis of purified DWNT-4-ATP-CdSe heterostructures, derived both covalently and non-covalently, as well as of purified DWNTs. (D) Raman profile of as-prepared CdSe QDs.

Collection of Raman Data at 785 nm

By means of comparison, Raman spectra of the aforementioned samples were also collected and measured at 785 nm (1.58 eV), and these data are shown in Figure S4. Specifically, spectra associated with pristine and purified DWNTs (Figure S4A) are similar to the analogous results measured at 514 nm (Figure 6A) with a perceptible increase in the I_D/I_G ratio after the acid treatment process (i.e. $I_D/I_G = 0.04$ for pristine DWNTs and 0.11 for the corresponding purified DWNTs). In order to probe the potential for charge transfer in these systems, the G band was studied prior to and after ‘doping’ with CdSe QDs at an excitation wavelength of 785 nm. Our G band profiles obtained at this particular wavelength appeared to be mainly associated with semiconducting nanotubes, based on the line shape, and are likely strongly influenced by small diameter inner semiconducting tubes.^{1,2} It is interesting to note that unlike at 514 nm excitation, we did not observe any appreciable shift in the positions of the Raman peaks at 785 nm excitation for all of the heterostructures analyzed (Figure S4B and C) upon CdSe QD attachment, using either noncovalent or covalent strategies.

We attribute the absence of shifts in the G bands noted at 785 nm excitation to either the total absence of or very minimal charge transfer, which could possibly have occurred for the following two reasons. First, shielding of the semiconducting inner tubes by the outer metallic tubes may have resulted in a very weak interaction between the inner semiconducting tubes and the attached CdSe QD ‘dopants’ and hence, a correspondingly smaller charge transfer effect between the two. That is, the inner semiconducting tubes are in stronger resonance and more prominent at this wavelength, and this fact contributes more to the observed line shape profile as opposed to any

nuanced charge transfer effect.² Second, the Raman spectrum of unbound CdSe QDs at 785 nm (Figure S4D) gave rise to a substantially noisier profile as compared with the results obtained at 514 nm (Figure 6D). Only a longitudinal optical phonon mode (1-LO) was clearly visible in the region of 200 cm⁻¹ with other peaks in the spectrum possibly emanating from the Si substrate background. No obvious fluorescence peak arising from bandgap emission in the 1000-3000 cm⁻¹ range was visible in the spectrum. The peak at 2500 cm⁻¹, corresponding to a feature located at 976.7 nm, could be possibly ascribed to an emission peak, emanating from trap states.

These observations are not surprising, considering that excitation either at 785 nm or at 1.58 eV represents an energy value which was far below the minimum energy level necessary for CdSe QDs to become truly photoexcited (Figure 6). Hence, the intrinsically low probability of finding charge carriers at 785 nm would have contributed to the low charge transfer observed. By contrast, at 514 nm, our more apparent observation of charge transfer was likely due in part to photoexcitation of the CdSe QDs themselves.

References

1. G. M. do Nascimento, T. Hou, Y. A. Kim, H. Muramatsu, T. Hayashi, M. Endo, N. Akuzawa and M. S. Dresselhaus, *Carbon*, 2011, **49**, 3585-3596.
2. A. G. Souza, M. Endo, H. Muramatsu, T. Hayashi, Y. A. Kim, E. B. Barros, N. Akuzawa, G. G. Samsonidze, R. Saito and M. S. Dresselhaus, *Phys Rev B*, 2006, **73**.