Electronic Supplementary Information (ESI) for:

Mechanism for Strong Binding of CdSe Quantum Dots to Multiwall Carbon Nanotubes for Solar Energy Harvesting

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1. Preparation of f-MWNT

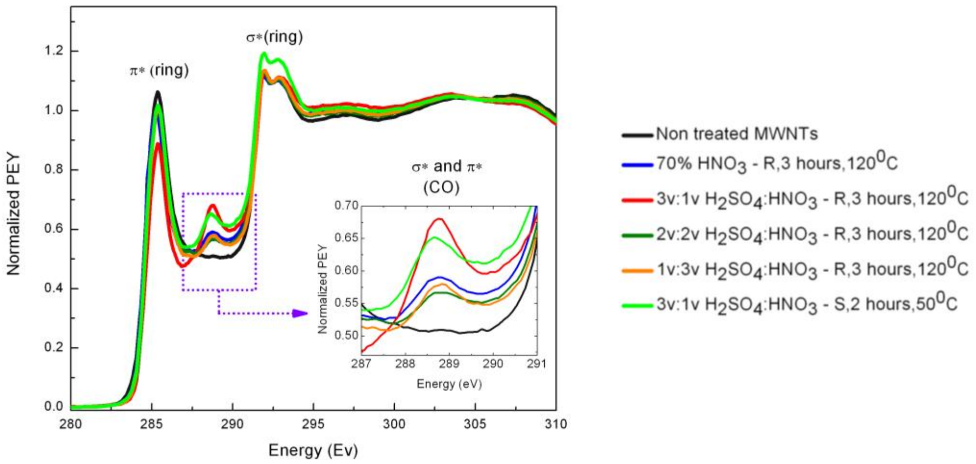

Figure S1. Carbon K edge NEXAFS spectra of MWNTs after different acid treatments (The corresponding treatment parameters are shown on the figure, where R stands for Reflux, and S for sonication. All the acids mixtures used were composed of concentrated acids.)

Figure S1 compares the measured Carbon K edge PEY signals for the different acid treated MWNTs. At the Carbon K edge, partial electron yield (PEY) data were collected at −40 V_{DC} bias and aligned to the π* transition at 285 eV of carbon reference. The π*(ring) transitions for all the samples are at around 285 eV and the σ*(ring) transitions are in the range from about 292 to 294 eV, consistent with that of the literature values.[1] The 287 - 290 eV region is where C-O bonding orbitals are detected. The C–O π* and C–O σ* transitions are assigned to 287.6 eV and 288.2 eV respectively.[1, 2] These transitions are unresolved, but it can be seen in Figure S1 that the MWNTs have C-O bonding after acid treatments whereas the non-treated MWNTs do not have detectable oxygen containing groups (OCGs). (The edge jumps of the spectra are normalized to unity to directly compare the intensity of C–O peaks.) Comparing the different treatments, it can be seen that the highest intensities of OCGs are obtained either by refluxing MWNTs with a 3:1 volume ratio of sulfuric acid nitric acid mixture for 3 hours at 120^{0}C, or by sonication of MWNTs with the same acid mixture for 2 hours at 50^{0}C.

Acid mixture sonication offers an additional benefit: TEM images obtained after both acid treatments show that it not only introduces OCGs, but also cuts the tubes. As received MWNTs are around 20-30 µm. After sulfuric acid: nitric acid mixture treatments, we have observed a drastic length reduction with the sonication method rather than the reflux when we observed the samples by TEM. (Figure S2b and c)

For the 3:1 acid mixture refluxed sample, it’s worth noting the intensity decrease in the C-C π* which results in an increase in the C-O bonding intensity. For the ultrasonication case though, when the same acid mixture was used to functionalize the MWNTs, the C-C π* intensity slightly decreased and intensities of both C-O and C-C σ* increased. The change in C-C π* can be explained with results from an earlier study [3] with the existence of concentrated sulfuric acid, producing electrophilic groups to attack this bond more efficiently. The study also talks about a possible change in the structure of carbon nanotubes as they observed a shift of the FTIR peak that is assigned to C-C π*. The increase in C-C σ*, on the other hand, can be a result of possible slight changes in the structure of MWNTs due to cutting.

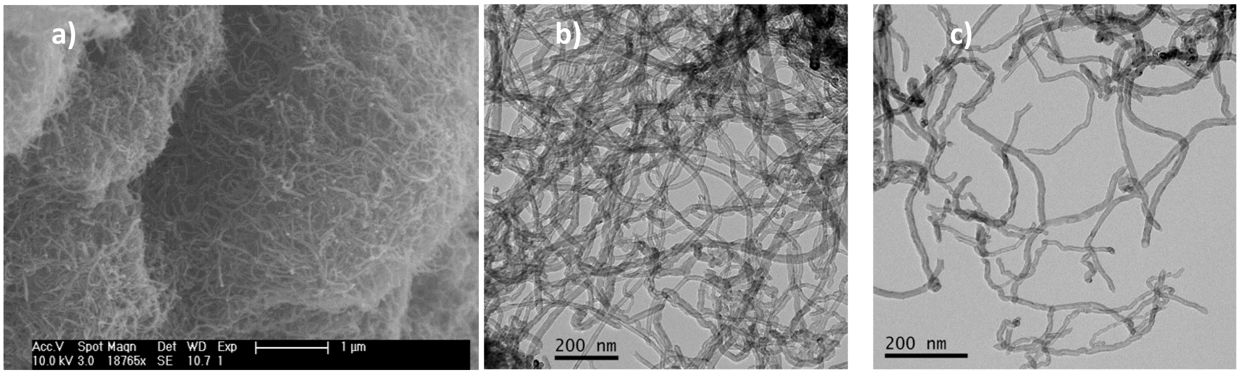

Figure S2. a) SEM image of HCl cleaned as received MWNTs (approximate length, 20-30 µm) TEM Imaged of b) H_2SO_4:HNO_3 (3:1 volume ratio) reflux of MWNTs at 120^{0}C for 3 hours c) H_2SO_4:HNO_3 (3:1 volume ratio) sonication of MWNTs at 50^{0}C for 2 hours.

2. CdSe Loading on the MWNT

2.1 Estimation of Cd and Se concentration using X-Ray Photoelectron Spectroscopy(XPS)

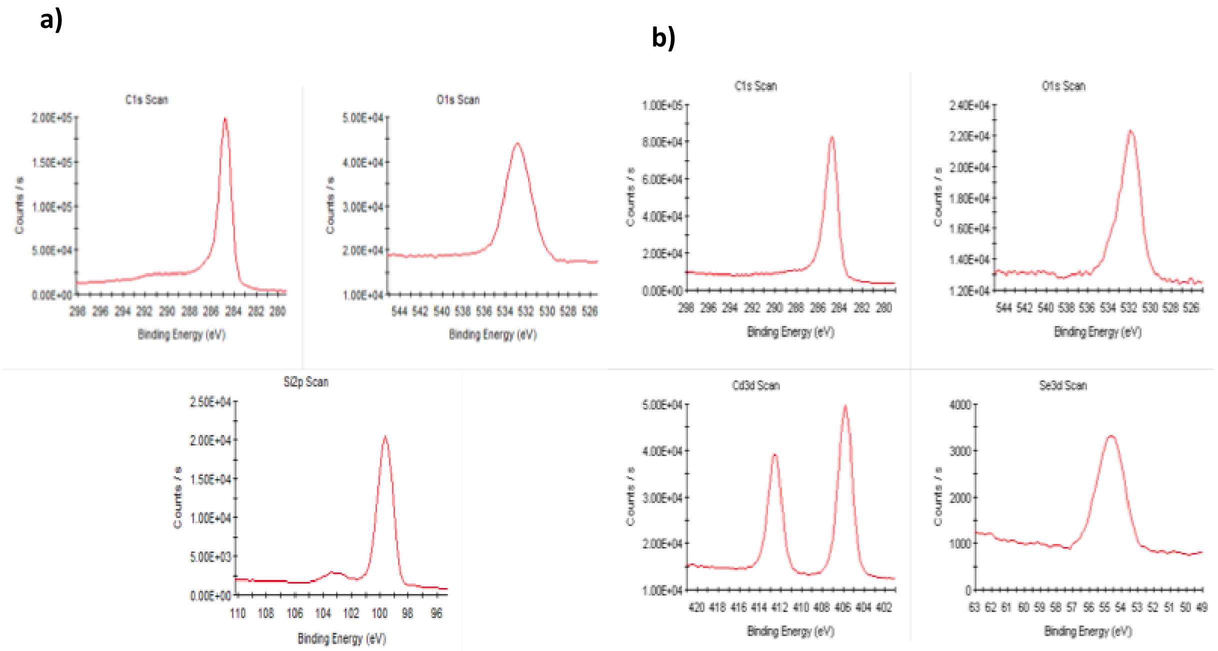

Figure S3. MWNT Sample: Detailed Scans/Composition a) functionalized MWNT b) CdSe-MWNT

XPS studies were performed to find out the CdSe loading on the MWNT samples. All spectra are taken on a Thermo Scientific ESCALAB 250 instrument at the University of Oregon. The samples are dispersed in ethanol and drop cast on the Si substrate. The pass energy was 50 eV for composition scans shown in Figure S3. Monochromatized Al X-ray source and 500 µm spot size was used for all the scans.

Table S1. Composition table showing atomic percent for the f-MWNT and CdSe-MWNT samples as compared to bare Silica substrate and non-functionalized MWNT

Sample	**C**	**O**	**Si**	**Cd**	**Se**
Si Substrate	16.3	8.5	74.8	**Not detected**	**Not detected**
MWNT	89.0	3.2	7.9	**Not detected**	**Not detected**
F-MWNT	84.0	7.3	8.6	**Not detected**	**Not detected**
CdSe-MWNT	88.0	6.1	0.7	3.6	1.5

The presence of Si arises from the Si substrate used to drop cast the powder samples on. Figure S3a shows the functionalized MWNTs and S3b shows the results from that of CdSe-MWNT heterostructure. Binding energy scales are adjusted in spectra plots for all samples. The Se binding energy, around 54 eV is consistent with CdSe.[4] Cd $3d_{5/2}$ peak position is around 405 eV, also consistent with that of literature values for CdSe.[4, 5] The results are tabulated together with the results of Si substrate and non-functionalized MWNT sample for comparison. (Table S1) “Not detected” means no detailed scan window was set for this element, and it was not observed in the survey scan. The atomic percentages of Cd and Se in the structure are 3.6% and 1.5 %, respectively. The weight percentages can be calculated as 25% Cd and 7% Se, rest of which being carbon, oxygen and trace amount of silicon. (62% Carbon, 5% Oxygen, 1% Si) This is in accordance with our initial CdSe loading on the carbon nanotubes.

3. Cd K Edge Fitting Results:

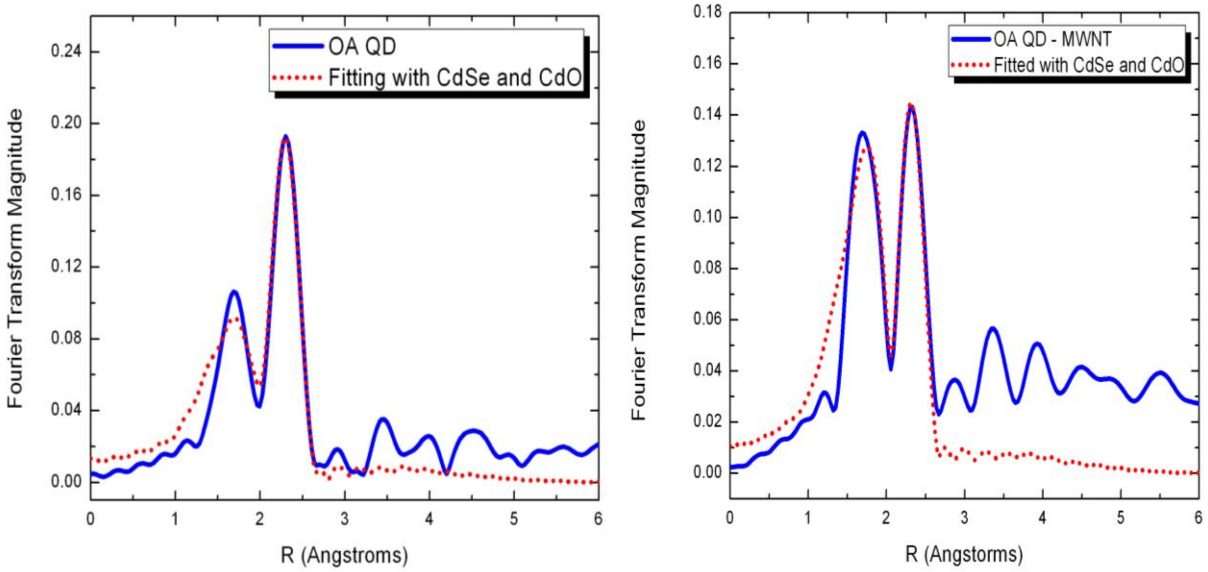

Figure S4. Radial Structure Distribution Functions of Cd obtained by Fourier transform of the k^1 weighted EXAFS functions (not phase corrected)

Table S2. Fitting results of the EXAFS data collected on the OA CdSe and CdSe-MWNT samples using the IFEFFIT program

Sample	Average Cd-Se First Shell Coordination Number	Cd-Se Bond Distance (A)	Mean Square Deviation in R	Average Cd-O First Shell Coordination Number	Cd-O Bond Distance (A)	Mean Square Deviation in R
OA CdSe QDs	3. 6 +/- 0.6	2.62	0.006	1.3 +/- 0.9	2.29	0.012
CdSe-MWNT	2.8 +/- 1.4	2.62	0.002	1.4 +/- 0.5	2.27	0.006
Crystallographic Data		2.62 [6]			2.34 [7]	

The first shell Cd-O and Cd-Se coordination numbers determined from the EXAFS data analysis are shown in Table S2. The two peaks are ascribed to the first shell oxygen and selenium neighbors at 2.3 and 2.6 Å, respectively. As a volume-sensitive technique, EXAFS reports coordination numbers as average between the scattering atoms in the bulk and at the surface. Each cadmium atom is surrounded with four Se atoms in the bulk, whereas the surface Cd atoms have different number of selenium neighbors. The average ratio of O to Se neighbors ranges between 0.1 and 0.7 for OA CdSe and that of CdSe-MWNT is between 0.1 and 1.1.

4. Carbon Edge Studies on MWNT-MWNT/CdSe

As explained in Section 1, the MWNTs have C-O bonding after they are functionalized with acids, whereas the non-treated MWNTs do not have detectable oxygen containing groups (OCGs). Comparing the functionalized MWNTs (f-MWNTs) and CdSe-MWNT heterostructure in Figure S5, we observe two notable phenomena. The intensity of the C-C π* peak decreases, resulting in an increase in the C-O bonding intensity. The change in C-C π* might mean a possible change in the carbon nanotubes structure due to coupling with the CdSe quantum dots. The inset shows a zoom up image for the C-O bonding range. We see that the peak gets very sharp and intensified in the case of CdSe-MWNT studies. It is hard to differentiate the COOH groups to conclude they belong to the carbon nanotubes or oleic acid in the Carbon K edge. That’s why a solid conclusion from Carbon K edge is not possible, however we can see the reflected changes in the Carbon edge. One good way of drawing more rigid results would be to obtain oleic acid spectra, but under high vacuum chamber XAS experiments, the liquid spectra is hard to obtain and analyze.

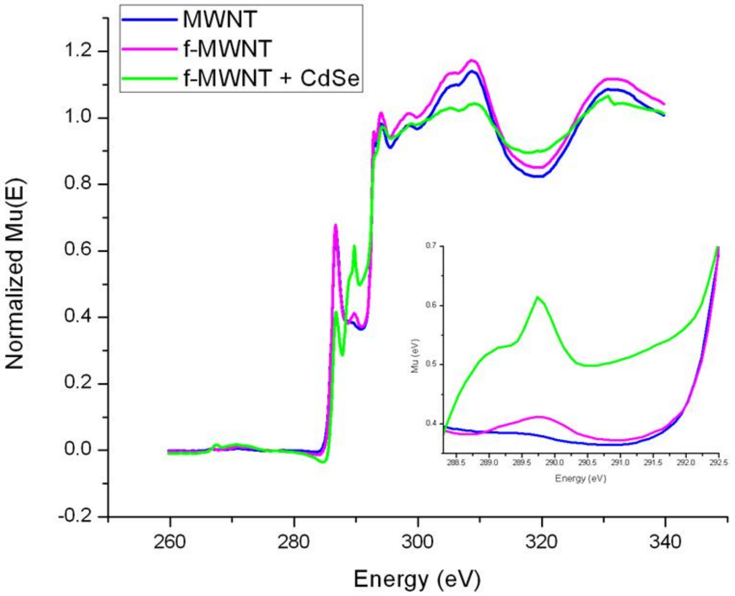

Figure S5. Carbon K edge NEXAFS spectra of MWNTs after functionalization (f-MWNTs) and CdSe attachment (f-MWNT+CdSe) (Inset shows the energy range corresponding to the C-O bonding)

5. Theory Calculations

5.1 Calculations of the Cd nearest neighboring atoms

Theoretical models are compared with experimental findings for the coordination numbers of the Cd atoms. For this the ratio of the number of Cd-Se to Cd-O bonds is calculated theoretically for various QD diameters. First, we note that the QD-OA binding does not involve charge transfer so that the OA coverage of the QD can become, in principle, quite high. The QDs in the theoretical model are constructed by starting with bulk wurtzite crystals, cutting out a spherical QD specified by a given diameter, and then removing all surface atoms with only a single-bond (i.e., a single nearest neighbor). The resulting surface atoms then have two or three bonds to atoms below them. To get the maximum coverage of the OA capping agents, we assume the surface Cd atoms are fully passivated and thus each Cd surface atom will have four bonds: either two or three Cd-O bonds formed with OA agents. We then count the number of Cd-O bonds and compare to the number of Cd-Se bonds. Figure S6 shows the Cd-O/Cd-Se ratio as a function of the QD diameter. As the average experimental diameter for the QD is around 3nm, the computations are done for the 2.0-4.5 nm diameter range. The ratio ranges between 0.1 and 0.25 substantiates the assumption of high capping agent coverage of the QD, is consistent with experiment, and is within the error limits of the EXAFS fit results. In order to see if there is a possibility that the Cd could oxidize and produce the Cd-O bonds, the TPO experiments are performed on OA capped QD and bulk CdSe samples. The results are discussed later in section 6 (Figure S7 and Figure S8).

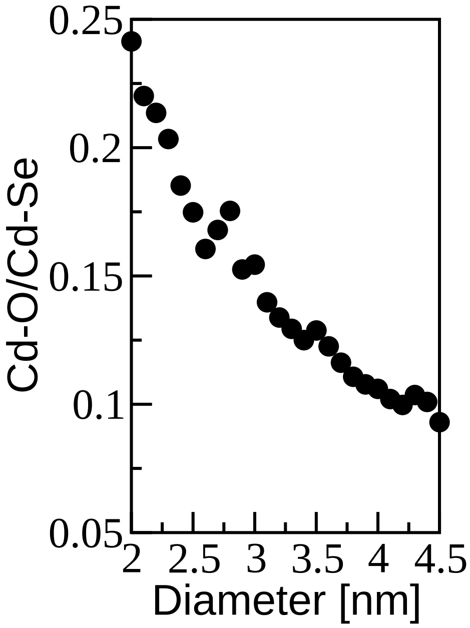

Figure S6. The ratio of the number of the Cd-O bonds to that of the Cd-Se bonds in CdSe QDs vs the QD diameter.

5.2 Interface Molecular Bonding Mechanism of CdSe/ Carboxylic Acid Group

As discussed in the main text, for both OA-CdSe and CdSe-MWNT bonding, the terminating oxygen atom in the functional -COOH group of the OA is covalently bounded to the Cd atom in the QD, and the hydrogen (from OH) in the functional group is weakly bound to the Se. The terminating oxygen starts in a closed shell configuration: its non-bonding p orbital contains two electrons and are right below in energy to the OA highest occupied molecular orbital. When the O-Cd bond forms, the O p orbitals and the Cd s orbital overlap to form a covalent bond. As the Cd is electron poor, the two O electrons are partially shared by the Cd to stabilize the bond. We note that if one tries to bond the terminating O to a surface Se, the O doesn't bind since the Se is electron rich. The computed O-Se binding energy is quite small (0.01 eV). When the Cd-O bond forms, the H in the ending OH group is weakly bound to a neighboring surface Se. This is because the H atom in the OH group is quite positively charged and electron poor which makes it bind to the negatively charged Se anion. This H-Se binding energy is not very large and is about 3/10 of O-Cd binding energy. Although theory predicts such a H-Se bond, we do not have access to a synchrotron X-ray absorption (XRA) spectrometer that could support this claim experimentally. Our present Se K edge results do not provide useful information on this matter (data not shown).

6. Temperature Programmed Oxidation (TPO) Results on the OA-CdSe QDs and Bulk CdSe Oxidation

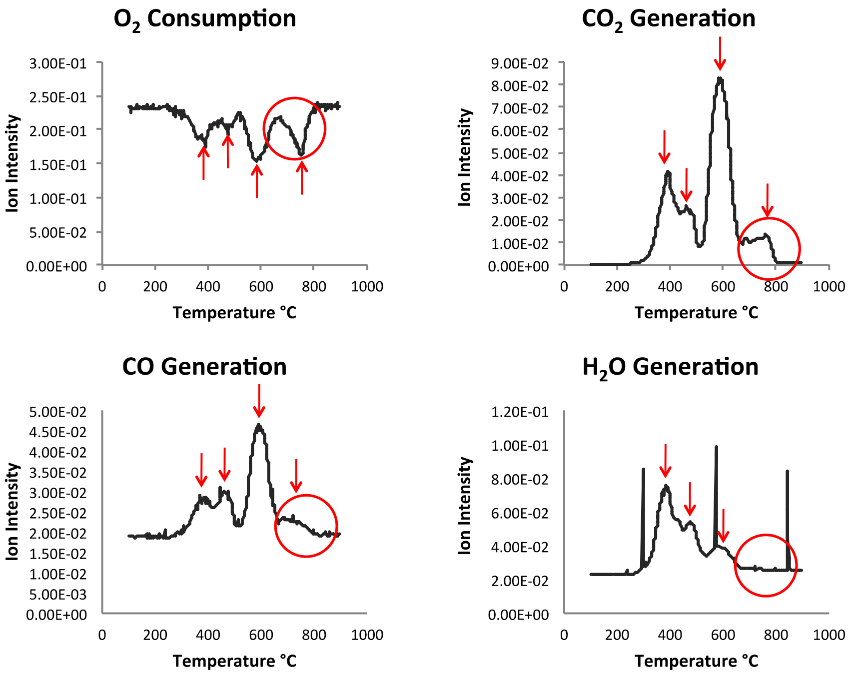

Figure S7. TPO profiles of oleic acid capped CdSe QDs; O_2 consumption, CO_2, CO and H_2O product signals are monitored during TPO.

Temperature-programmed oxidation (TPO) experiments were performed in the same way of TPD by only changing the flowing gas to 5% O_2 in He.

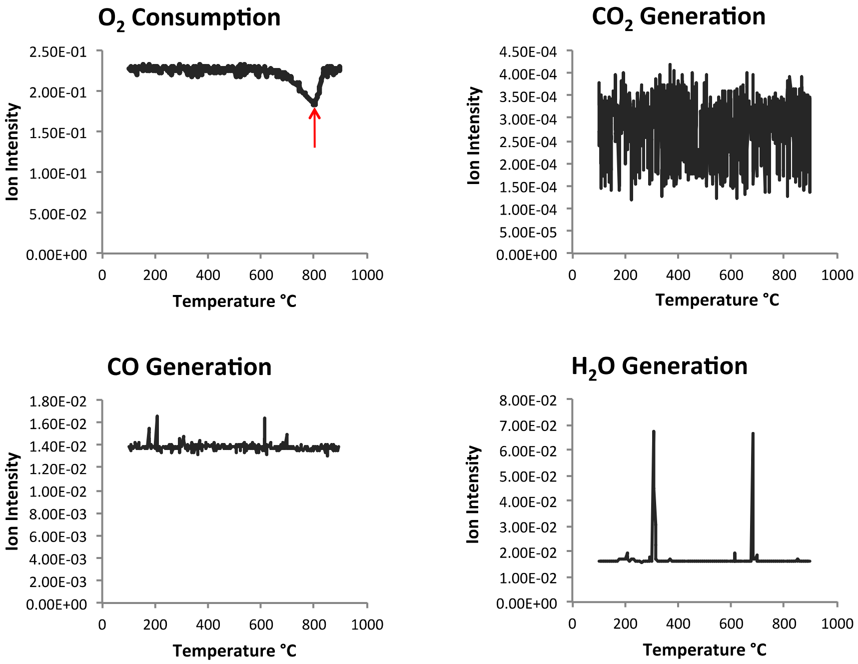

Figure S8. TPO profiles of bulk CdSe; O_2 consumption, CO_2, CO and H_2O product signals are monitored during TPO.

The lower oxidation temperatures for the OA capped CdSe QDs correspond to the oxidation of oleic acid groups as they are producing H_2O, CO_2 and CO. (Figure S6) However, at 800^0C, the amount of CO_2 and CO production is significantly lower and no H_2O production is observed although the O_2 was still being consumed. This suggests that the CdSe starts to oxidize at this temperature. When the same experiment is performed on the bulk CdSe sample, the temperature at which oxygen consumption starts was found also to be 800^0 C as expected. (Figure S7) Therefore, we can safely say that the Cd-O coordination number from EXAFS studies would arise only when Cd group from the CdSe makes a bond with oxygen groups from either oleic acid or COOH MWNTs as the CdSe does not oxidize below 800^0C.

References

1. A. Kuznetsova, I. Popova, J. T. Yates, M. J. Bronikowski, C. B. Huffman, J. Liu, R. E. Smalley, H. H. Hwu and J. G. G. Chen, *J Am Chem Soc*, 2001, **123**, 10699-10704.

2. S. Banerjee, T. Hemraj-Benny, M. Balasubramanian, D. A. Fischer, J. A. Misewich and S. S. Wong, *Chemphyschem*, 2004, **5**, 1416-1422.

3. J. Zhang, H. L. Zou, Q. Qing, Y. L. Yang, Q. W. Li, Z. F. Liu, X. Y. Guo and Z. L. Du, *J Phys Chem B*, 2003, **107**, 3712-3718.

4. E. Agostinelli, C. Battistoni, D. Fiorani and G. Mattogno, *J Phys Chem Solids*, 1989, **50**, 269-272.

5. J. E. B. Katari, V. L. Colvin and A. P. Alivisatos, *J Phys Chem-Us*, 1994, **98**, 4109-4117.

6. J. C. Bailar and A. F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry Pergamon*, New York, 1973.

7. I. N. Demchenko, J. D. Denlinger, M. Chernyshova, K. M. Yu, D. T. Speaks, P. Olalde-Velasco, O. Hemmers, W. Walukiewicz, A. Derkachova and K. Lawniczak-Jablonska, *Phys Rev B*, 2010, **82**.