Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

Charge Carrier Cascade in Type II CdSe/CdTe Graded Core-Shell Interface

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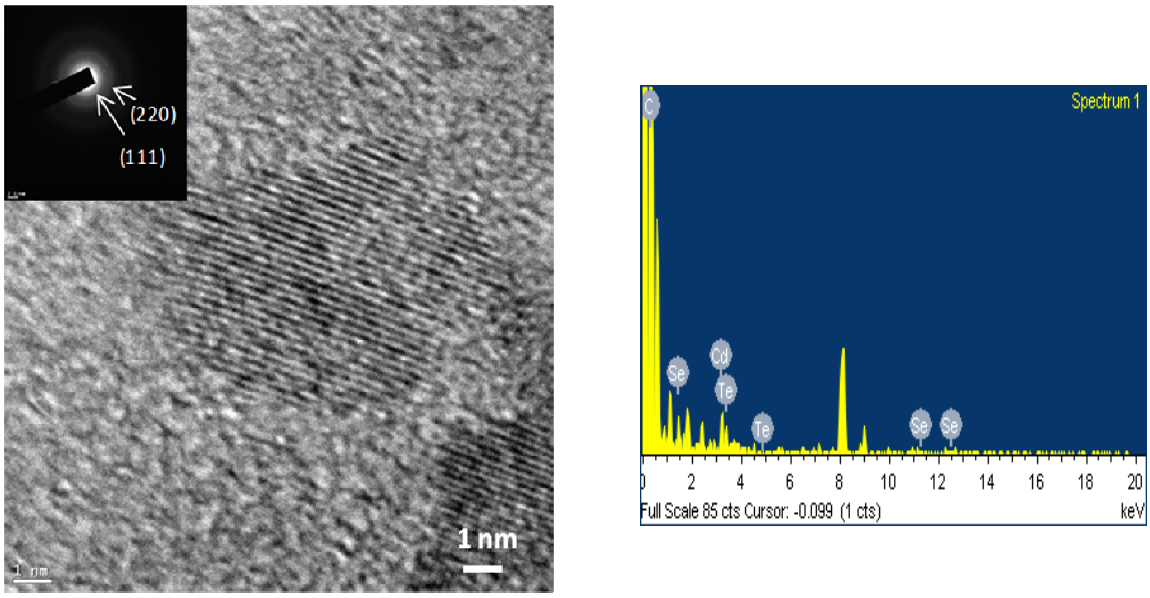
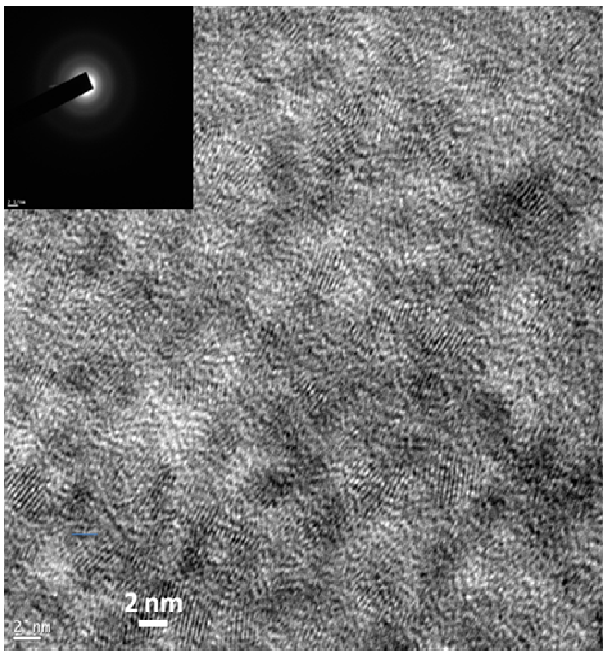
1. Transmission Electron Microscope Measurements:



SI Figure 1: HRTEM Images of CdSe-3G. Inset: SAED Patterns of the representative samples. In the right panel EDAX spectrum has been shown.



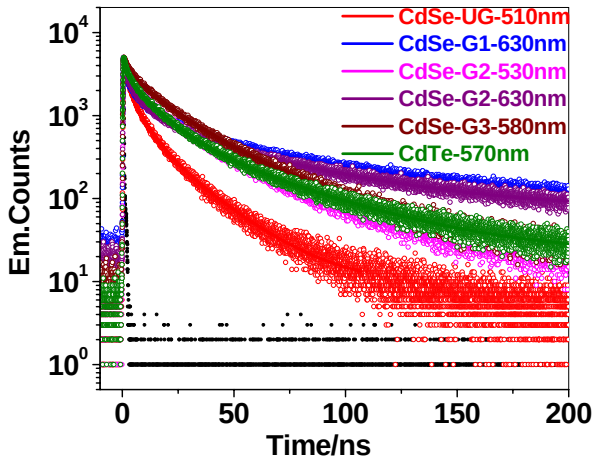
SI Figure 2: HRTEM Images of CdSe-UG. Inset: SAED Patterns of the representative samples.

2. Emission Spectroscopy:

Steady state absorption and emission spectroscopy and time-resolved emission has been carried out for CdSe QD, CdSe/CdTe Graded core-shellwith different shell composition and CdSe/CdTe ungraded core-shell.

SI Table 1: The Excition Absorption ($\lambda_{exciton}$) position, PL (λ_{PL}) peak position and Emission Quantum Yield for Core and Core Shell Samples.

Sample	$\lambda_{exciton}$	λ_{PL} (Peak Wavelengths)	Quantum Yield
CdSe-0	462	635	0.5
CdSe-G1	463	530, 618	0.2
CdSe-G2	465	533, 618	0.3
CdSe-G3	490	566	0.9
CdSe-CdTe UG	480	520	0.3



SI Figure 3: Time-resolved emission decay kinetics of CdTe QD, and CdTe/CdSe graded core-shell (different shell composition) and ungraded core-shell at different wavelenghts. The wavelengths are selected at both exciton peak and at surface state emission peak

SI Table 2: Fits of PL Decay kinetics monitored at the peak wavelengths for the individual samples. Note: Peak wavelengths are also given in the figures. $\tau_{avg} = \frac{\sum_{i=1}^{3} a_i \tau_i^2}{\sum_{i=1}^{3} a_i \tau_i}$

Sample	λ_{PL} (Peak Wavelengths)	Decay Times (% Contribution), ns			
		τ_1	τ_2	τ_3	τ_{av}, ns
CdSe-0 (Our previous	620 nm	0.5 (59)	3.8 (34)	17.4 (7)	2.8
CdSe-G1	618 nm	1.3 (5.1)	10.4 (24)	58 (70.9)	55.2
CdSe-G2	533 nm	2 (7)	12 (43)	38 (50)	32.3
	618	1.4 (6.7)	10.7 (28)	55 (65.3)	51.5
CdSe-G3	570 nm	3.7 (6.7)	16.6 (49)	42.5	34.4
CdSe-UG	520 nm (Exciton)	1.4 (12.3)	6.3 (41)	20.5 (46.7)	17.2

3. Calculation of Valence and conduction band edges of CdSe quantum dots with respect to vacuum

$$\begin{pmatrix} E_{VB} = -5.23 - 0.74 d^{-0.95} \\ E_{CB}^{opt} = -3.59 + 1.79 d^{-1.62} \end{pmatrix} \qquad (1)$$

E_{VB} is the shift in valence band position, E_{CB}^{opt} is the shift in conduction band position and d is the diameter of the quantum dots in nanometers.

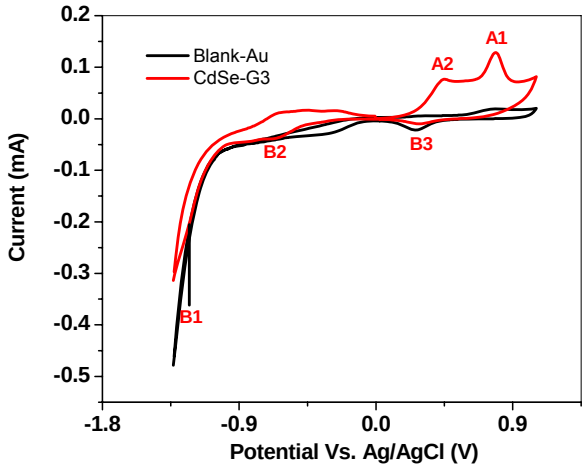
The band positions of CdSe with respect to vacuum is,

$$E_{VB} = -5.61 eV$$

$$E_{CB}^{opt} = -3.01 eV$$

4. Cyclic Voltametric measurements on Graded Core-Shell:

Cyclic Voltammograms of bare Au and CdTe-G3 sample in buffer solution as described in experimental section.



SI Figure 4: Cyclic Voltammograms of bare Au and CdTe-G3 sample in buffer solution as described in experimental section.

To assign the alignment of levels between the core and shell we carried out cyclic voltammetry measurements on CdSe-G3 core shell sample. For the CdSe core we have arrived at the VB and CB positions [1] as described above. The VB and CB positions derived by Jasieniak et al [1] are fairly accurate and matches well with results from high level theoretical studies. The VB & CB positions from CV was arrived at as described previously [2]. SI Figure 4 shows CV of blank with Au working electrode. Anodic peak at ~0.7V corresponds to oxidation of Au electrode. CV of QD was recorded with QD concentration of few μM. The CV shows several reduction and oxidation features in the potential region scanned. The A positions are correspond to the anodic features and B positions are correspond to the cathodic features. Since the sample is core shell the electron transfer takes place at the surface the anodic and cathodic features corresponds to the redox reaction occurring at the shell. The band alignment of the shell can be arrived at from CVs. The anodic peaks A2 was previously assigned to oxidation of midgap defects. The A1 appearing at 0.65V onset of oxidation peak was assigned to oxidation of CdTe (shell) surface. According to previous studies it was found that this peak only showed a small shift with respect to size of CdTe essentially underestimating position of the VB [2]. This feature could be assigned to

oxidation of CdTe. Based on these values we can arrive at VB position of CdTe with respect to vacuum to be -5.3V. To arrive at the CB values we match the VB level with the data for CdTe as arrived by Jasieniak et al [1]. We find from the extrapolation that the CB level of CdTe shell is ~-2eV. In the case of CdSe core VB and CB positions are -5.61eV and -3.01eV respectively as obtained from Jasieniak et al [1]. This provides additional evidence of formation of a Type II graded interface. Interestingly we observe that the VB alignment between the two semiconductors show just ~0.16eV difference. The number of monolayers for each shell material is the same for all the three core shell nanostructures formed i.e. CdSe-G1, CdSeG2 and CdSe-G3. Therefore difference mainly in the VB and CB alignment will be governed by mole fractions of Se:Te. The material with larger Se mole fraction i.e. CdSe-G1 will be expected to have VB alignment close to CdSe. We had previously hypothesised that VB alignment shift on increasing Te mole fraction to explain disappearance of trap emission arising from thiol states on surface even though comprising monolayers are similar. The present CV and experimental measurement by Jasieniak et al [1] clearly authenticates that hypothesis.

5. Calculation of strain from Raman Frequency Shift

$$\frac{\Delta\omega}{\omega} = \left(1 + 3\frac{\Delta a}{a}\right)^{-\gamma} - 1 \qquad (2)$$

In the above equation, γ is the Gruneisen parameter and a is the lattice parameter.

γ=1.1 for CdSe. ω is Raman shift for core sample and $\Delta\omega$ is the change in raman shift on formation of shell.

$\left(\frac{\Delta a}{a}\right)$=0.009

SI References

1. Jacek Jasieniak, Marco Califano, and Scott E. Watkins, *ACS Nano*, **2011**, 5, 588.
2. Poznyak, S. K. Nikolai P. Osipovich, Alexey Shavel, Dmitri V. Talapin, Mingyuan Gao, Alexander Eychmuller and Nikolai Gaponik, J. Phys. Chem. B, 2005, 109, 1094.