Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information.

S1. Transmission Electron Microscopy

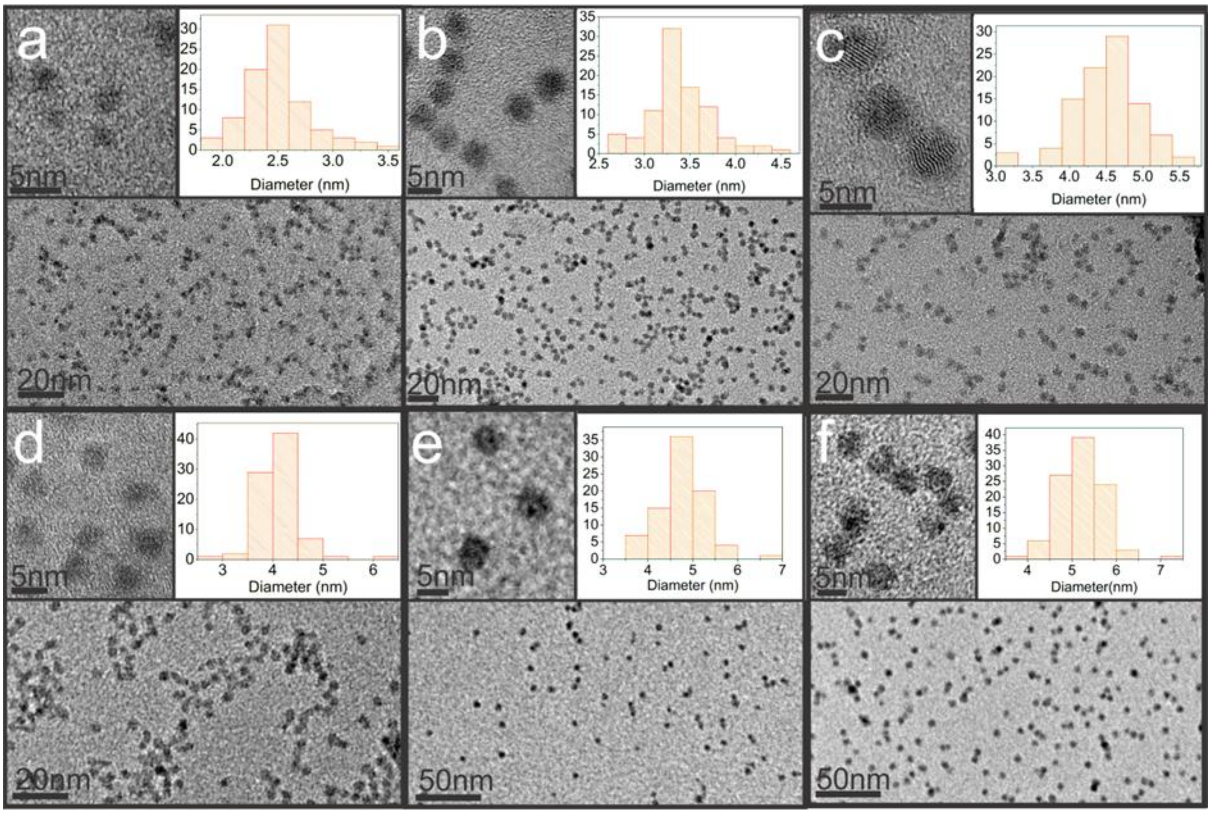

Figure S1. Transmission electron micrographs for the a) 2.4nm core, b) 2.4nm core and 2ML shell c) 2.4nm core and 4ML shell d) 4.1nm core e) 4.1nm core and 1ML shell, and f) 4.1nm core and 2ML shell ZnTe/ZnSe CQDs. Inset are high resolution images of the CQD and size histograms.(Images a) to c) are also included in Ref.23)

S2. Shell Thickness Calculations.

The shell thickness, t_s, for each of the core/shell structures was calculated, in terms of a number of monolayers, by:

$$t_s = \left(\frac{d_{cs} - d_c}{2}\right)\frac{2}{a} \tag{S1}$$

where d_{cs} and d_c are the respective diameters of the core and core/shell structures, as measured by TEM, and a is the lattice constant for ZnSe (Ref 24 in main manuscript); no compression of the core was assumed.

S3. Characterisation by Powder X-ray Diffraction (XRD).

The NQD were characterised by XRD using a Philips PW 1830 diffractometer with a Cu Kα source. Fig S3 compares the results for a ZnTe core and two ZnTe/ZnSe core/shell samples. The data shows a consistent zinc blende structure which shifts from the bulk ZnTe diffraction pattern towards the ZnSe. The associated lattice constants are 6.10A, 6.07A and 5.85A for the ZnTe core, 4.1nm ZnTe core/ 2ML ZnSe shell and 2.4nm ZnTe core/ 4ML ZnSe shell samples, respectively. The larger shift in lattice constant to ZnSe for the 2.4nm ZnTe core/ 4ML ZnSe shell sample is consistent with a larger ZnSe volume fraction.

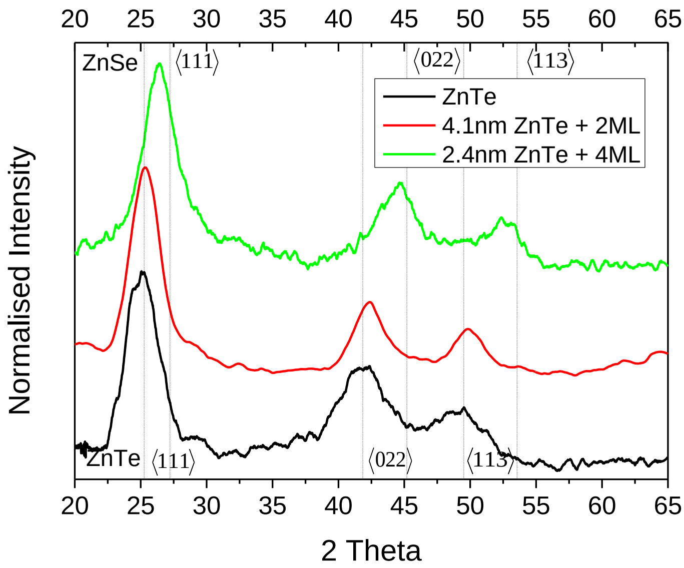

Figure S2. *A comparison of the XRD powder diffraction patterns of ZnTe cores (Black), 4.1nm diameter cores + 2ML shell (Red) and 2.4 nm diameter cores +4ML shell(Green). The bulk diffraction peaks of ZnTe and ZnSe are highlighted at the bottom and top of the plot respectively.*

S4. Determination of Carrier Localisation.

The most common approach to define the carrier localisation regime in a theoretical context is by using the `energy criterion'[24]. For the case of ZnTe/ZnSe, the type-II region is defined where the electron $1s^{(e)}_{3/2}$ single particle energy falls below the conduction band of the core and the hole $1S^{(h)}_{1/2}$ single particle energy remains in the core. The quasi type-II regime can be defined where one single particle energy is localised in the core and the other is localised over the whole NC region. The strain-incorporating model described in Ref. 23 was used to single particle energies for each of the four ZnTe/ZnSe NQD samples studied, which are shown in figures S3 and S4. Comparison of these energy levels with the conduction band minima and valance band maxima (also shown in figures S3 and S4) allows us to conclude that, according to the energy criterion: the 2.4 nm core/4ML shell and

4.1 nm core/2ML shell NQDs are both type-II; the 4.1 nm core/ 1ML shell NQD is quasi-type-II; and the 2.4nm core/2ML shell NQD is on the border between the two regimes.

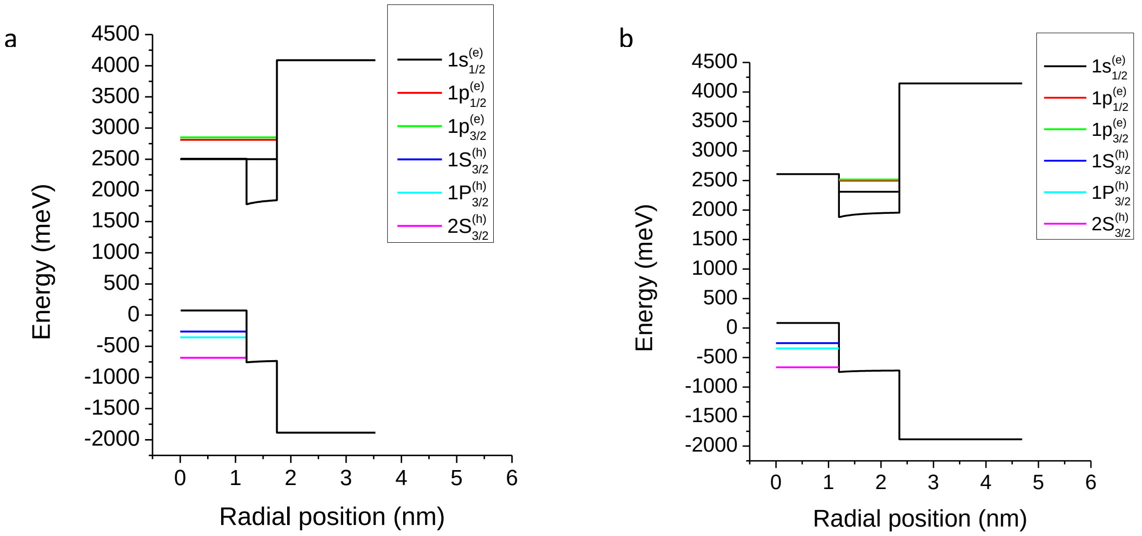

Figure S3 The valence and conduction band and the associated $1s(e)_{1/2}$, $1p(e)_{1/2}$, $1p(e)_{3/2}$ $1S(h)_{3/2}$, $1P(h)_{3/2}$ and $2S(h)_{3/2}$ energy levels for a 2.4nm diameter ZnTe core with a) 2ML ZnSe and b) 4 ML ZnSe shell

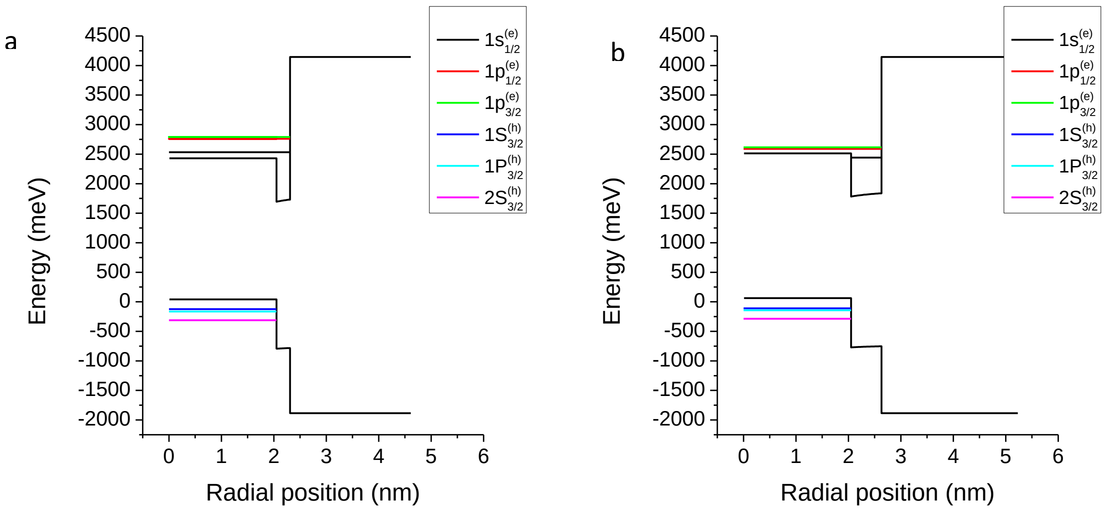

Figure S4. The valence and conduction band and the associated $1s(e)_{1/2}$, $1p(e)_{1/2}$, $1p(e)_{3/2}$, $1S(h)_{3/2}$, $1P(h)_{3/2}$ and $2S(h)_{3/2}$ energy levels for a 4.1nm diameter ZnTe core with a) 1ML ZnSe and b) 2ML ZnSe shell.

S5. Pump-induced fractional transmittance transients.

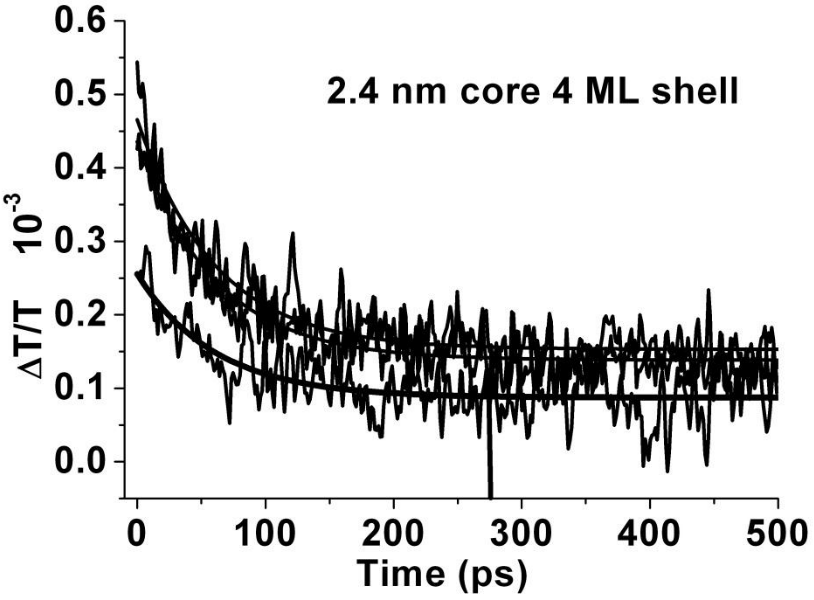

Fig. S3 Pump-induced fractional transmittance transients for the 2.4 nm ZnTe core / 4ML ZnSe shell CQDs for pump powers ranging between 0.5 and 2mW. The fits shown are to a single exponential decay function.

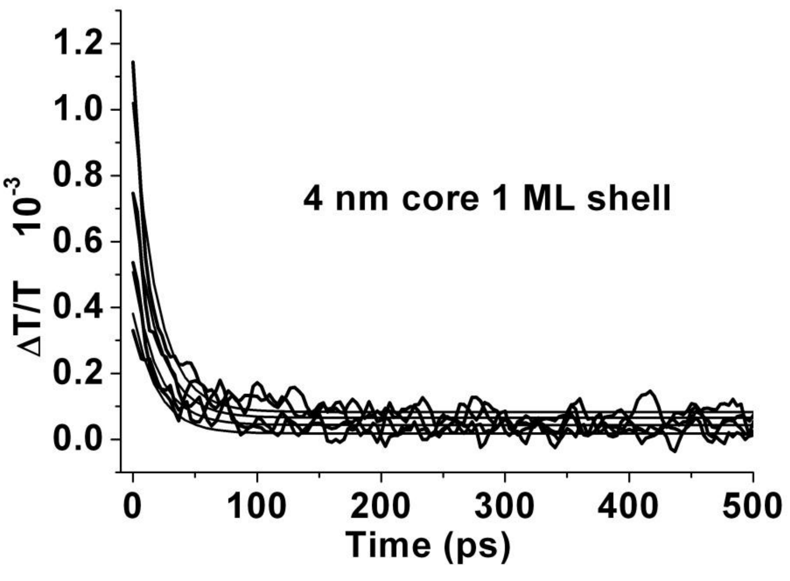

Fig. S4 Pump-induced fractional transmittance transients for the 4 nm ZnTe core / 1ML ZnSe shell CQDs for pump powers ranging between 0.5 and 1.5 mW. The fits shown are to a single exponential decay function.

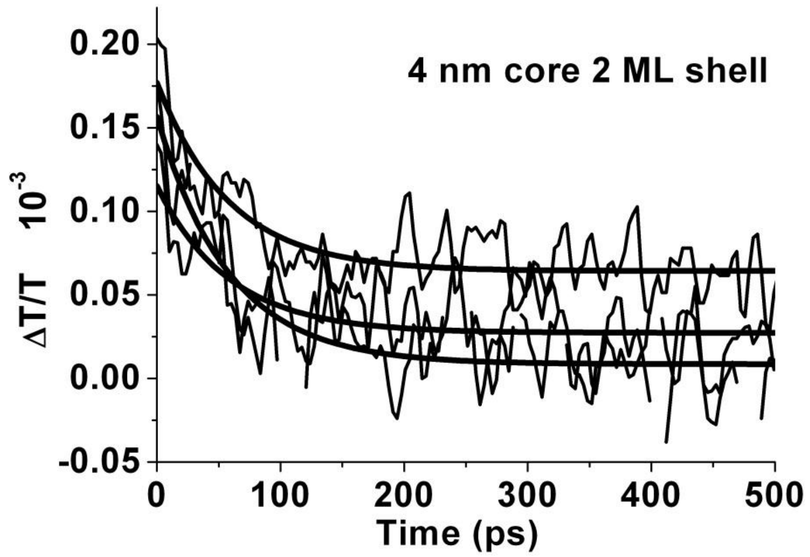

Fig. S5 Pump-induced fractional transmittance transients for the 4 nm ZnTe core / 2ML ZnSe shell CQDs for pump powers ranging between 0.5 and 3 mW. The fits shown are to a single exponential decay function.

S6 Fractional transmittance spectra.

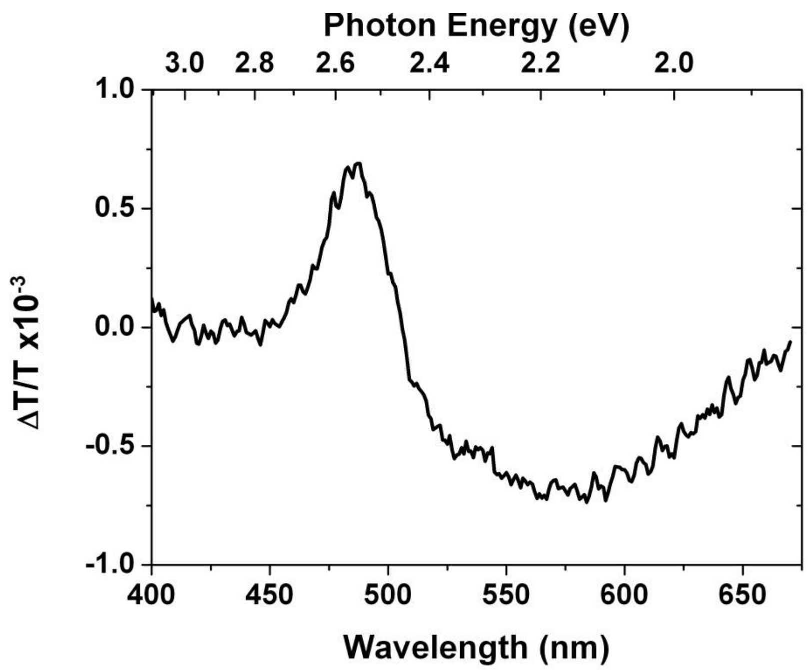

Fig S6 Fractional transmittance spectra ~3 ps after the pump pulse for the 2.4 nm ZnTe core CQD with 2 ML ZnSe shell and a pump power of 1 mW.

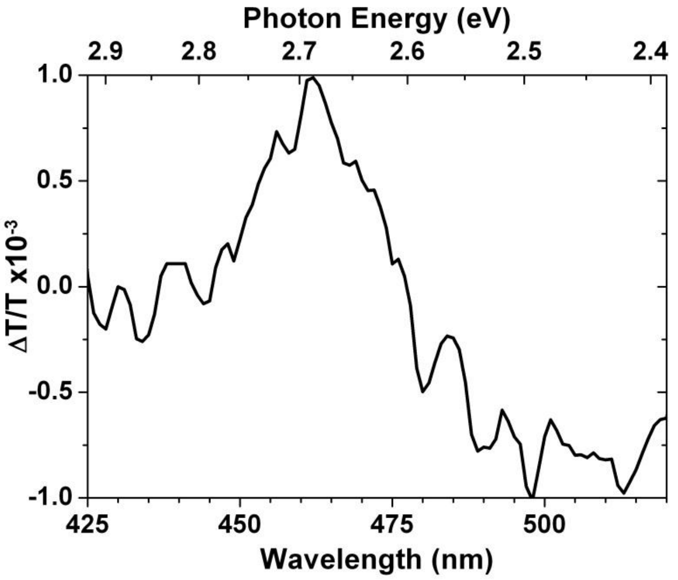

Fig S6 Fractional transmittance spectra ~3 ps after the pump pulse for the the 4 nm ZnTe core CQD with 1 ML ZnSe shell for a pump power of 1 mW.

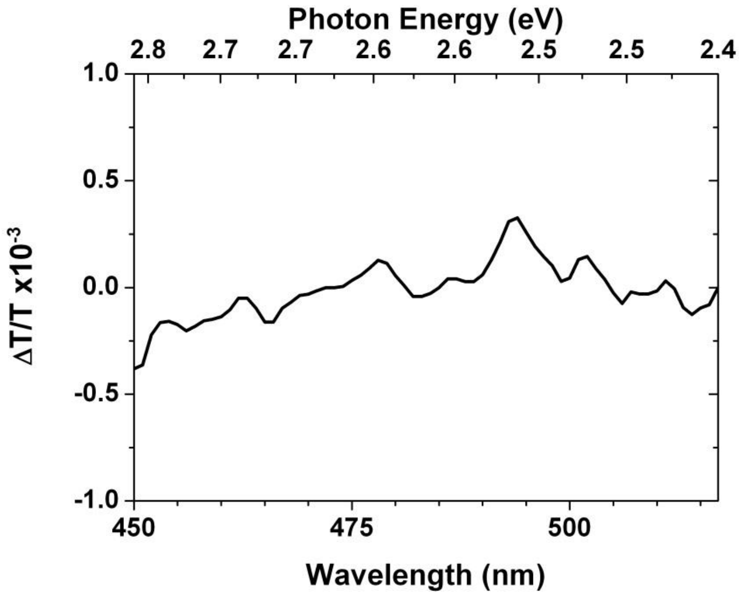

Fig S6 Fractional transmittance spectra ~3 ps after the pump pulse for the the 4 nm ZnTe core CQD with 2 ML ZnSe shell for a pump power of 1 mW.