<p align="center">**Supporting Information**</p>

<p align="center">**Ultrafast Charge Carrier dynamics in CdSe/V$_2$O$_5$ core/shell Quantum Dots**</p>

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S.1 TEM images and confirmation of core/shell nanostructure

Figure S.1 (a-c) shows TEM micrographs of CdSe, CdSe/V$_2$O$_5$ (Thin) and CdSe/V$_2$O$_5$ (Thick) core/shell QDs, respectively. Figure S.1 (a-c) depict that QDs are spherical in shape, mono-dispersed and crystalline in nature. The diameters were calculated as 3, 4.5 and 6 nm for CdSe core, CdSe/V$_2$O$_5$ (Thin) and CdSe/V$_2$O$_5$ (Thick) core/shell QDs, respectively as shown in inset image of figure S.1 (a-c). High crystallinity and monodispersity of CdSe/V$_2$O$_5$ core/shell QDs ruling out any separate nucleation of V$_2$O$_5$ with CdSe. Further, the PL intensity of CdSe/V$_2$O$_5$ (Thin) and CdSe/V$_2$O$_5$ (Thick) core/shell QDs increases dramatically in comparison to CdSe QDs (Figure S.1d). It represents better passivation of CdSe surface defect states due to core/shell formation. Symmetrical and Single emission band in emission spectra exclude any possibility of alloys formation.

Moreover, we have carried out the synthesis of CdSe QDs at a different time interval (1-12 h). In this experiment an interval of 1h, CdSe QDs solution was taken out from the reaction mixture and stored for PL measurement in toluene solution.
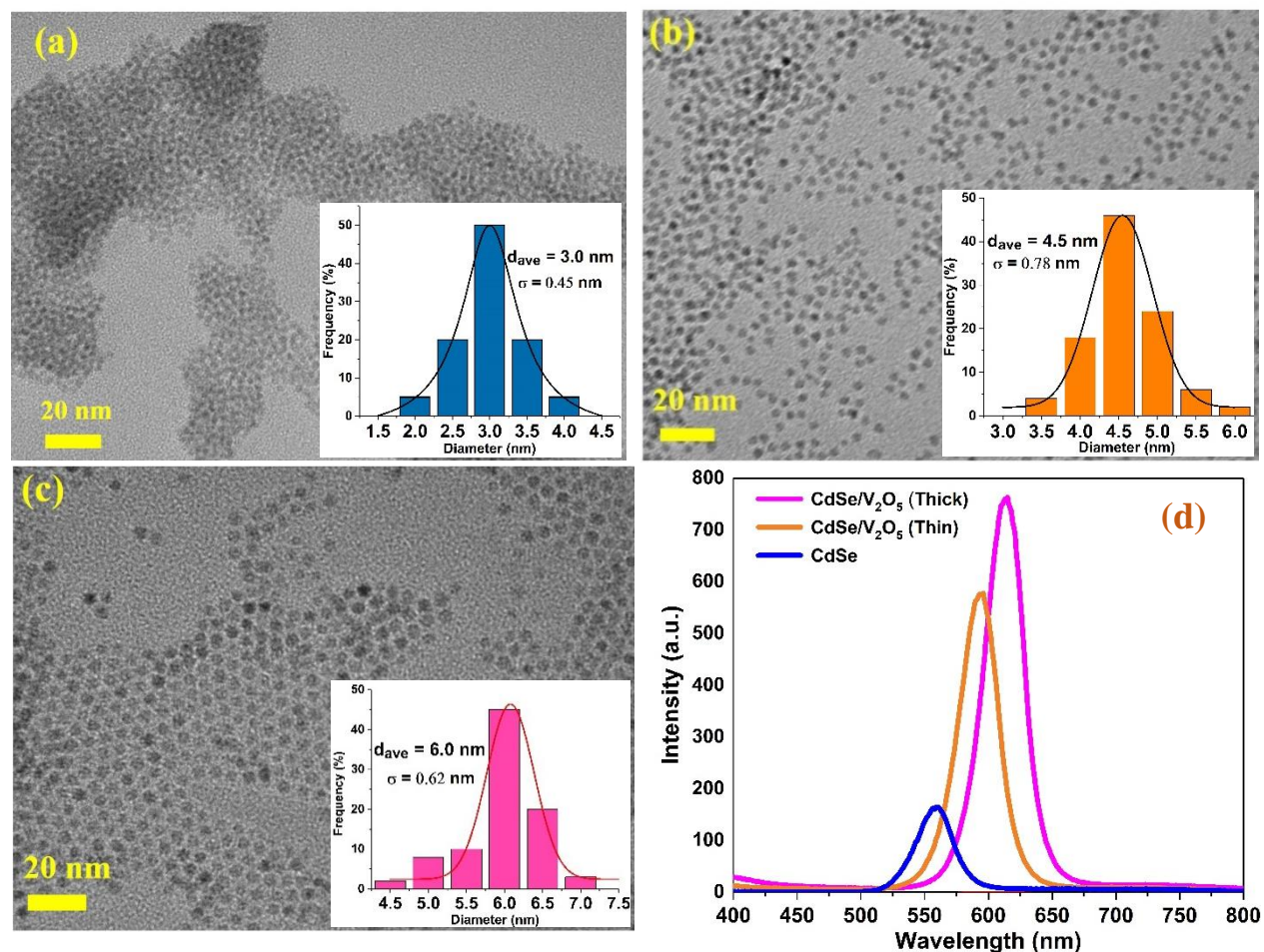

Figure S.1 TEM micrographs (a) CdSe QDs, (b) CdSe/V_2O_5 (Thin), and (c) CdSe/V_2O_5 (Thick) core/shell QDs. Inset image of a-c is particles size distribution where d_{ave} and σ denote mean diameter and its standard deviation (d) PL spectra of CdSe, CdSe/V_2O_5 (Thin) and CdSe/V_2O_5 (Thick) core/shell QDs.

Figure S.2 shows PL spectra of CdSe QDs at different interval of reaction time. It is clear from the figure that the PL spectra of CdSe get red-shifted (maximum at 565 nm) up to 8 h of reaction time, after that there is no significant shift in the PL spectra. Also, it observed from figure S1 (d) that

the PL spectra of core/shell structure that is very different from the core structure. The redshift in the PL spectra of core/shell structure occurs with increasing shell thickness and peak wavelength have been found at 595 and 615 nm for thin and thick core/shell QDs, respectively. Therefore, we can conclude that the additional redshift observed in the case of core/shell structure is due to shell formation on CdSe core not from its size (CdSe) effect[1].
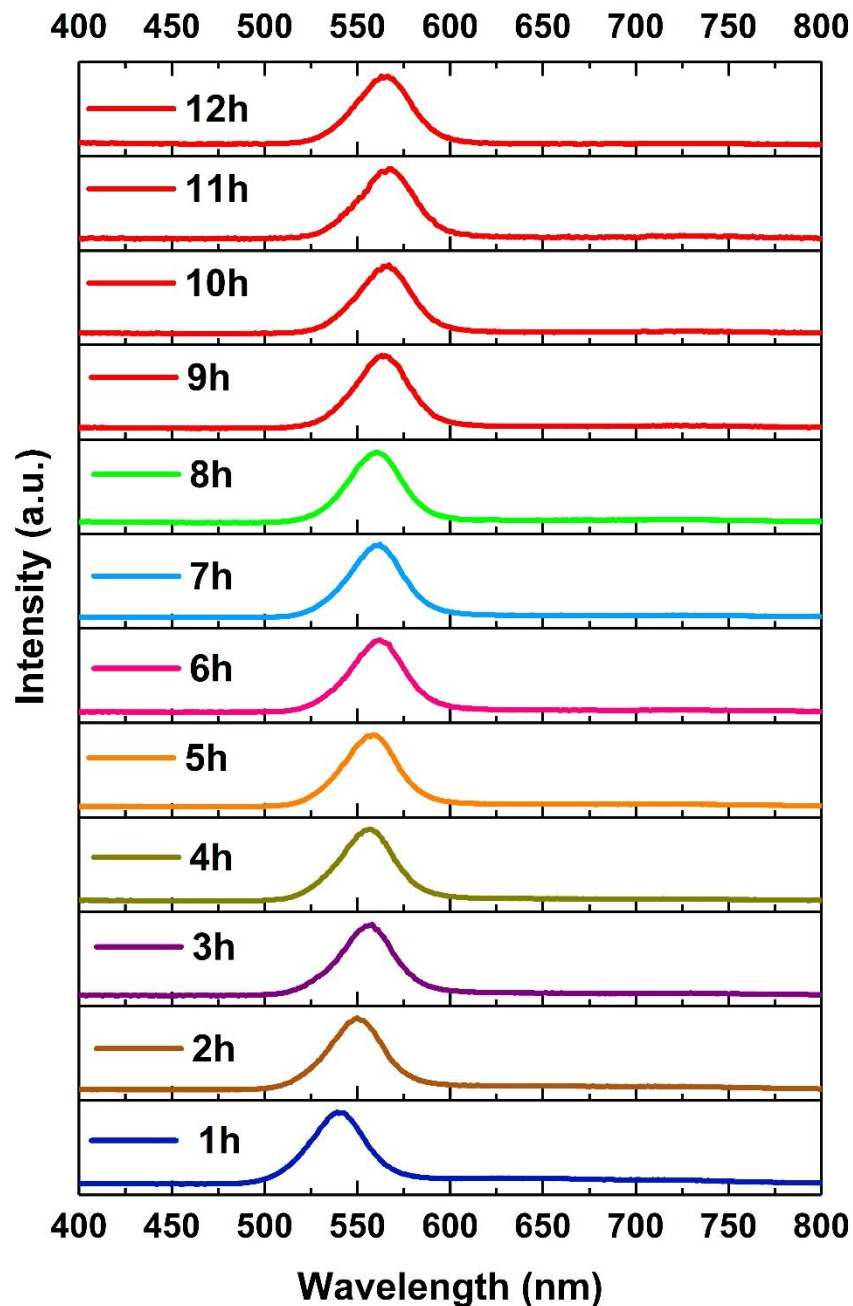

Figure S.2 PL spectra of CdSe QDs at different reaction time (1-12 hrs.), $\lambda_{exc}=$ 310 nm

S.2 Determination of average lifetime and Fluorescence Quantum Yield (QY)

The PL decay curves of core and core/shell QDs can be well fitted with a bi-exponential function, using the following equation[2]

$$Y(\tau) = a_1 \, e^{\frac{-\tau}{\tau_1}} + a_2 \, e^{\frac{-\tau}{\tau_2}}$$

The average lifetime of all samples calculated by

$$\tau_{ave} = \frac{a_1 \tau_1^2 + a_2 \tau_2^2}{a_1 \tau_1 + a_2 \tau_2}$$

Where τ_1 and τ_2 are the first and second component of decay time, a_1 and a_2 are corresponding amplitudes.

Table S.1 Summary of bi-exponential decay fit components and corresponding their average lifetime

Samples	τ_1 (ns)	τ_2 (ns)	τ_{ave} (ns)
CdSe	2.31 (66%)	24.41 (34%)	22±1
CdSe/V$_2$O$_5$ (Thin)	2.06 (57%)	38.62 (43%)	36±2
CdSe/V$_2$O$_5$ (Thick)	2.05 (41%)	46.84 (59%)	46±3

Calculations of Fluorescence Quantum Yield (QY)

The fluorescence QY of all QDs were obtained by using a comparative method[3]. We have used Rhodamine 6G dye (R6G) as the standard for the QY correction. The R6G ($QY_R = 95\%$) was dissolved in ethanol (Refractive index of ethanol, $n_R = 1.360$) and all QDs were dissolved in toluene (Refractive index of toluene, $n_X = 1.496$). The intensity of the first absorption peak of R6G dye and all QDs were adjusted to 0.05 and then steady state emission spectra recorded using same

excitation wavelength (λ_{exc} = 480 nm) to find their relative intensities. Finally, the QY value (Q_X) found by using the following equation

$$Q_X = Q_R \cdot \frac{A_R}{A_X} \cdot \frac{F_X}{F_R} \cdot \left(\frac{n_X}{n_R}\right)^2$$

Where Q_R is the standard QY, F is the emission intensity; n is the refractive index of the solution.

S.3 Calculation of Lattice Mismatch[4]

Lattice Mismatch between core and shell calculated by using (101) planes of CdSe (Wurtzite structure)[5] and V_2O_5 (Orthorhombic structure)[6] by formula

$$\% \text{ Lattice Mismatch} = 100 \times \left[\frac{d_{(101)}^{CdSe} - d_{(101)}^{V2O5}}{d_{(101)}^{CdSe}} \right]$$

Further, the lattice mismatch has been found to be ~14% in this case.

S.4 Marcus Theory Analysis [7-9]

The reorganization energy is

$\lambda_{CdSe\ or\ CS} = \frac{1}{2}\Delta v$, where Δv is stokes shift

Table S.2 Summary of observed energetics from deconvoluted absorption and emission spectra of CdSe/V_2O_5 (thin) core/shell QDs

Sample	A_{CdSe}	A_{CS}	E_{CdSe}^{Max}	E_{CS}^{Max}	λ_{CdSe}	λ_{CS}
CdSe/V_2O_5 (Thin)	556 nm 2.230 eV	583 nm 2.126 eV	590 nm 2.101 eV	595 nm 2.084 eV	0.064 eV	0.021 eV

The ground state (GS) potential energy is

$G_{GS}(x) = \frac{1}{2}Kx^2$,

Free energy curves are

$$G^{NA}_i(x) = K\frac{(x-a)^2}{2} + \Delta G^0_i,$$

Where K is spring constant set to be unity for arbitrary units of x (bath polarization). NA is stand for Non-adiabatic, i = CdSe or CS,

$a_i = \sqrt{2}\lambda_i$, so that $a_{CdSe} = 0.359$ eV and $a_{CS} = 0.204$ eV

ΔG^0_i is free energy difference between ground state and excited state i, and calculated as

$$\Delta G^0_{CdSe} = A_{CdSe} - \lambda_{CdSe} = 2.165 \text{ eV}$$

$$\Delta G^0_{CS} = A_{CS} - \lambda_{CS} = 2.105 \text{ eV}$$

$$\Delta G^0_{ET} = \Delta G^0_{CS} - \Delta G^0_{CdSe} = 0.060 \text{ eV} = -60 \text{ meV} \pm 10 \text{ meV}$$

Further, $G^{NA}_{CdSe}(x) = \frac{(x-0.34)^2}{2} + 2.165,$

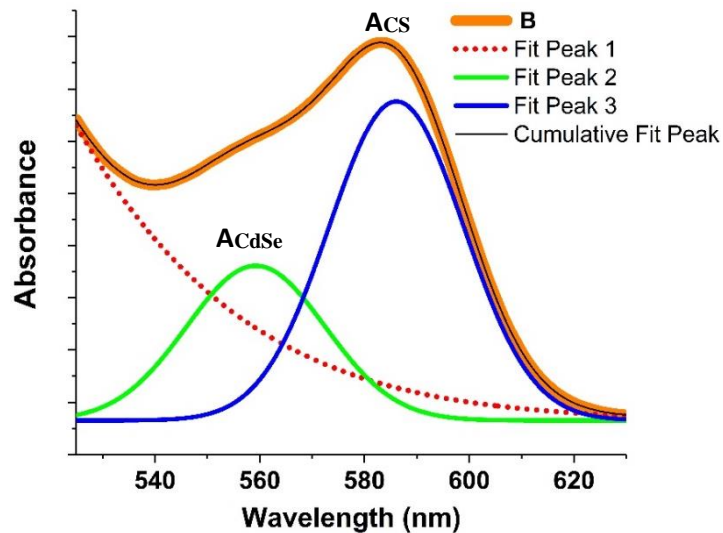$$G^{NA}_{CS}(x) = \frac{(x-0.2)^2}{2} + 2.105$$

Figure S.3 Deconvoluted absorption spectrum of CdSe/V_2O_5 (Thin) core/shell QDs. It gives two band one at 556 nm assign as A_{CdSe} and other at 583 denoted as A_{CS}. The other dotted Gaussian line needed for fitting and has no physical meaning.

S.5 Adiabatic Analysis

In absorption, the oscillator strength of CS state is slightly higher than CdSe, while in emission the CdSe peak is broader than CS states. The reason behind is there is strong mixing between these two states (CS and CdSe states). Therefore, we have carried out adiabatic analysis to show strong mixing between these two states. The two potential energy curves cut each other due to strong mixing .

The transfer integral (V) given as[10]

$$V = \frac{A_{CdSe} - A_{CS}}{2} \sim 52 \text{ meV}$$

The adiabatic curves are

$$G^A_1(x) = G^{NA}_{CdSe}(x) + V \tan \eta$$

$$G^A_2(x) = G^{NA}_{CS}(x) - V \tan \eta$$

Where $\eta = \frac{1}{2} \tan^{-1} [2V / G^{NA}_{CdSe}(x) - G^{NA}_{CS}(x)]$

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