Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Hot-Electron Transfer from Semiconductor Domain to Metal Domain in CdSe@CdS{Au} Nano-Heterostructure

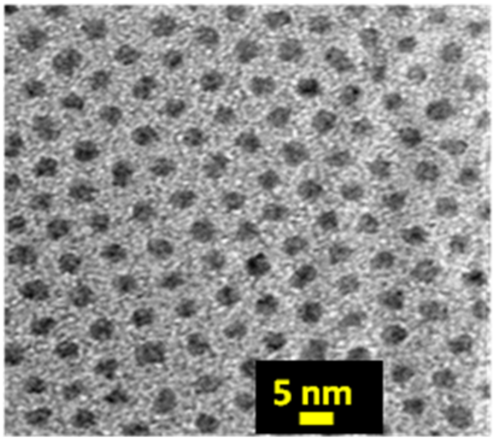
Jayanta Dana,[a] Partha Maity,[a] and Hirendra N. Ghosh[a,b,*]

[a]Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Homi Bhabha National Instutute, Mumbai-400085, India.

[a,b]Institute of Nano Science & Technology, Mohali, Punjab – 160062, India

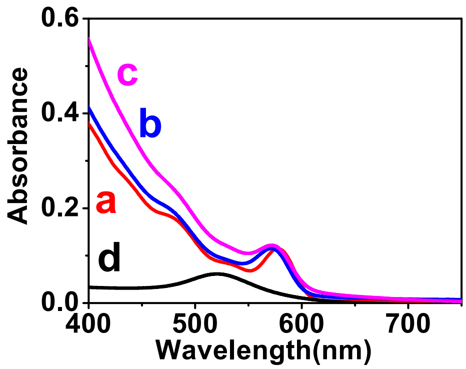
* To whom correspondence should be addressed. E-mail: hnghosh@barc.gov.in, Fax: (+) 91-22-25505331/25505151

1. HR-TEM images of CdSe@CdS core shell :



SI Figure 1. The HR-TEM shows the size of CdSe@CdS is ~3.5 nm.

2. Comparison of Steady State Optical Absorption Spectra of Core Shell, Hetero-structures and Isolated Au NPs.

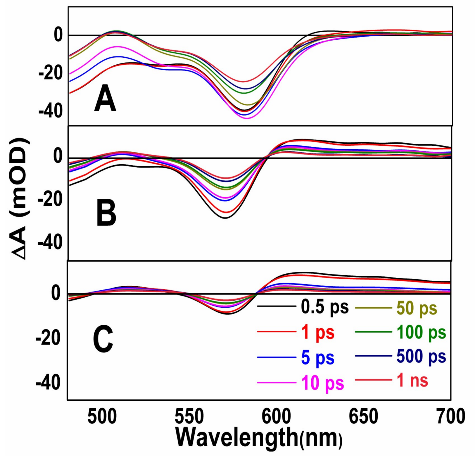


SI Figure 2. UV-Visible steady state optical absorption spectra of (a) CdSe@CdS core shell (b) CdSe@CdS{Au}-1 (c) CdSe@CdS{Au}-2 nanohybrid materials and (d) isolated Au NP (~5 nm) in chloroform solvent.

OD correction:

We have already mentioned that the charge transfer processes is responsible due to light absorbed by CdSe/CdSe core-shell in the CdSe@CdS-Au hetero-structure. We have carried out all the transient absorption studies by exciting the samples at 400 nm where both Au NP and CdSe@CdS core-shell absorbs light in the hetero-structure. The transient spectra presented in Figure 2 we kept same optical density (OD) at 400 and then multiplied by the multiplication factors by which CdSe@CdS core-shell absorb similar intensity of light. The un-normalized spectra are reported below.

Before OD correction:



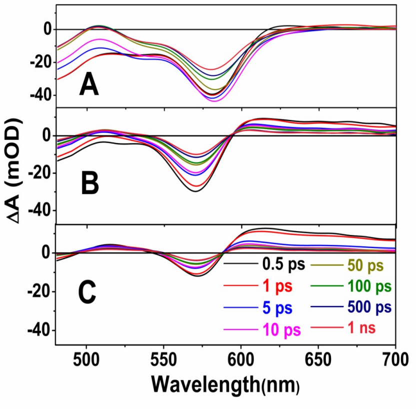
SI Figure 3. Transient Absorption spectra of (A) CdSe@CdS core shell nanoparticles (B) HS 1 hetero-structure and (C) HS 2 hetero-structure materials after exciting the samples at 400 nm and keeping same optical density.

Now OD at 400 nm is 0.37 and 0.55 for pure CdSe/CdS core shell and CdSe@CdS{Au}-2 nanohybrid respectively i.e ~33% photon absorbed by Au NP in the hetero-structure at 400 nm .

Similarly 7% photon is absorbed by Au in HS 1.

Therefore HS 1 and HS 2 spectra are multiplied by 1.07 and 1.33 respectively to get real contribution by core shell in the spectral intensity, have been shown below and shown in the main manuscript.

After OD correction:



SI Figure 4. Transient Absorption spectra of (A) CdSe@CdS core shell nanoparticles (B) HS 1 hetero-structure and (C) HS 2 hetero-structure materials after multiplying proper multiplication factor in spectra B and Spectra C.

3. Calculation of average no. of exciton (<N>).

$$<N>= \sigma . j$$

j~ Pump fluency, i.e. no. of photon per cm^2 and $\sigma= (4/3)\, \pi\, |f|^2\, \alpha\, R^3$

α ~ bulk absorption co-efficient, $|f|^2$ ~ co-efficient for local field effect (~0.25)

Excitation energy of 400 nm Pump = 0.4 μJ

Thus, $nh\nu= 0.4 \times 10^{-6}$ J

$h= 6.626 \times 10^{-34}$ J s and $\nu= c/\lambda = (3 \times 10^{8}\ ms^{-1})/(400 \times 10^{-9}\ m)$

Hence, $n \sim 8 \times 10^{11}$

Beam diameter~ 300 μm

Therefore,

Pump fluency, i.e. no. of photon per cm^2 is the order of ~ $11*10^{14}\ cm^{-2}$

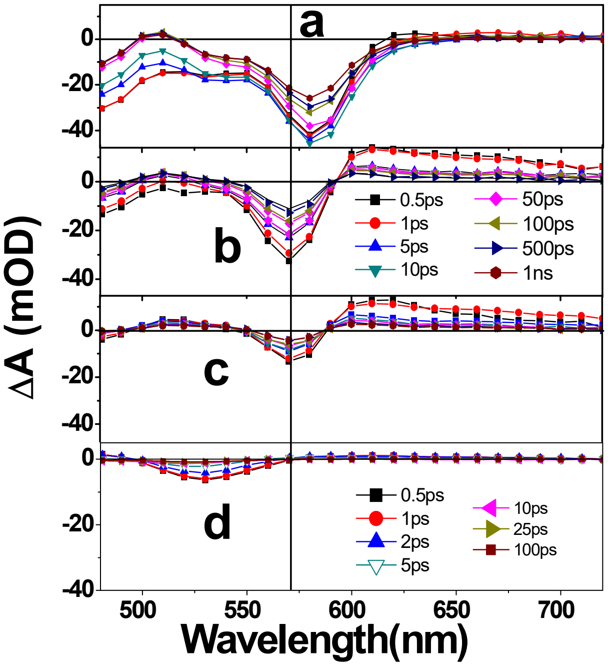
So radius, R =1.75 nm

$\alpha \sim 1.5*10^5\ cm^{-1}$

$\sigma = 0.28*10^{-15}\ cm^2$

$<N> \sim 0.3$

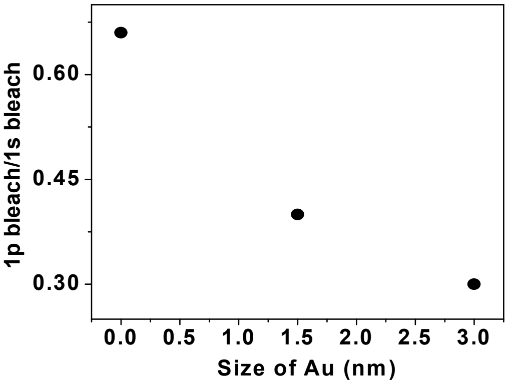
4. Comparison of TA Spectra of Core Shell, Hetero-structure and Isolated Au NPs.



SI Figure 5. Transient Absorption spectra of (a) CdSe@CdS core shell nanoparticles and (b) CdSe@CdS{Au}

1 (c) CdSe@CdS{Au} 2 nanohybrid material and (d) isolated Au NP (~5 nm) in chloroform as solvent after 400 nm laser excitation.

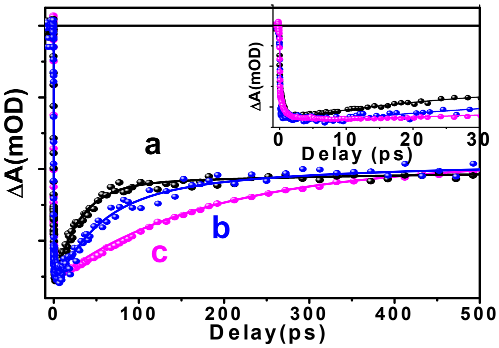
5. Bleach ratio of 1p/1s in TA spectra of CdSe@CdS{Au} 1 and CdSe@CdS{Au} 2 .



SI Figure 6. Bleach ratio of 1p/1s in CdSe@CdS{Au} hetero-structure with Au particle size.

6. Carrier Cooling Dynamics in CdSe@CdS Quasi type II Core-shell.

Ultrafast transient absorption spectroscopic studies have been carried out for CdSe QD, CdSe@CdS and CdSe@CdS 1 cre-shells to see the effect of charge carrier dynamics on shell thickness, where the thickness of CdS shell are 2 ML and 6 ML in CdSe@CdS and CdSe@CdS 1 respectively. Bleach dynamics at 1st excitonic position for all the above systems were monitored. It's interesting to see that the 1st exciton bleach gradually red shifted to 600 nm for CdSe@CdS 1 from CdSe 570 nm and shown in figure below. SI Figure 7 a, b, and c represent the bleach dynamics for CdSe at 570 nm, CdSe@CdS at 580 nm and for CdSe@CdS 1 at 600 nm, respectively. The growth components for CdSe and CdSe@CdS are <100 fs (75%), 0.5 ps (25%) and <100 fs (75%), 3 ps (25%), respectively. Interestingly for CdSe@CdS 1 core shell growth kinetics can be fitted with time constants of <100 fs (75%), 1 ps (21%) and 9 ps (4%). i.e. the growth components gradually increases with increasing the CdS shell thickness (Inset of SI Figure 7). These results indicate the delocalisation of electron throughout the conduction band of CdS shell which increases with the shell thickness. Thiese observation clearly suggests due to smaller band off set of the conduction bands of CdSe and CdS photo-excited electrons are delocalized in the CB of in both the QDs making an ideal system of quasi-type II core shell. This band off set decreases with increasing CdS thickness as a result carrier cooling time increases with thickness in CdSe@CdS 1. The bleach recovery kinetics also slows down with increasing the thickness of CdS shell as seen in figure below (SI Figure 7, SI Table 1). Increasing the electron cooling and recombination time with shell thickness clearly suggests decoupling of electron from hole due to quasi type-II band structure.



SI Figure 7: Bleach dynamics of (a) CdSe at 570 nm, (b) CdSe@CdS at 580 nm and (c) CdSe@CdS 1 at 600 nm. **In Inset.** Early scale bleach kinetics of a, b, and c.

SI Table 1: Multi-exponential fitted parameters of the decay kinetics of CdSe, CdSe@CdS and CdSe@CdS 1 core shell.

System @wavelength	τ_{g1} (%)	τ_{g2} (%)	τ_{g3} (%)	τ_1 (%)	τ_2 (%)	τ_3 (%)
CdSe-570nm	<100fs (75%)	500fs (25%)		30 ps (-37%)	150ps (-4%)	>500 ps (-59%)
CdSe@CdS2ML-578 nm	<100fs (75%)	3ps (25%)		50 ps (-36%)	250 ps (-6%)	>500 ps (-58%)
CdSe@CdS6ML-600 nm	<100fs (75%)	1ps (71%)	9 ps (4%)	150 ps (-42%)	>500 ps (-58%)	

7. a. SI Table 2: Multi exponential fitted parameter of luminescence decay traces of CdSe@CdS, CdSe@CdS{Au}-1 and CdSe@CdS{Au}-2 after exciting the samples at 445 nm and monitoring at 596 nm.

System	τ_1	τ_2	τ_3	τ_{avg}
CdSe@CdS	3.61 ns (55%)	22.9 ns (45%)		12.28 ns
CdSe@CdS{Au}-1	0.045ns(93%)	1.23ns(5%)	9.31ns(2%)	0.29 ns
CdSe@CdS{Au}-2	0.04ns(88%)	0.6ns(9%)	3.83ns(3%)	0.2 ns

b. SI Table 3: Multi-exponential fitted parameters of the decay kinetics at 1S and 1P excitonic bleaches of CdSe@CdS core shell, CdSe@CdS{Au}-1 and CdSe@CdS{Au}-2 hetero-structures.

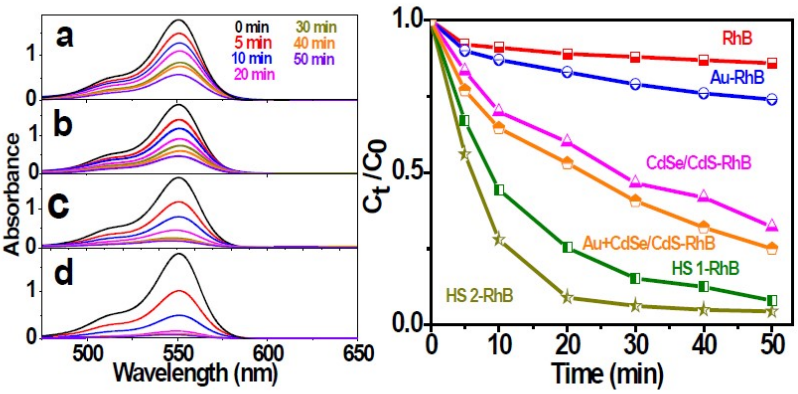
System@λ_{nm}	$\tau_{1(growth)}$	$\tau_{2(growth)}$	τ_1	τ_2	τ_3	τ_4
CdSe/CdS@ 580 nm	<100 fs (86%)	3 ps (14%)	50 ps (-36%)	250 ps (-6%)	>1 ns (-58%)	
AuCdSe/CdS-1 @570 nm	<100 fs		550 fs (-22%)	10 ps (-25%)	150 ps (-12%)	>1 ns (-41%)
AuCdSe/CdS-2 @570 nm	<100 fs		300 fs (-24%)	3 ps (-24%)	40 ps (-16%)	>1 ns (-36%)
CdSe/CdS @480 nm	<100fs (90%)	0.15ps (10%)	9ps (-67%)	60ps (-11%)	>1 ns (-22%)	
CdSe/CdS{Au}-1 @480 nm	<100fs		300 fs (-45%)	3.5ps (-27%)	160ps (-15%)	>1ns (-13%)
CdSe/CdS{Au}-2 @480 nm	<100fs		150 fs (-68%)	1.5 ps (-17%)	170ps (-12%)	>1 ns (-3%)

C. SI Table 4: The multi-exponential fitted parameters of decay kinetics of CdSe@CdS{Au}-1 and CdSe@CdS{Au}-2 hetero-structures.

System@λ_{nm}	$\tau_{1(growth)}$	τ_1(%)	τ_2(%)	τ_3(%)

CdSe/CdS{Au}-1 @620 nm	150 fs	0.95ps (-67%)	40 ps (-18%)	>1 ns (-15%)
CdSe/CdS{Au}-2 @620 nm	140 fs	0.95ps (-67%)	38 ps (-20%)	>1 ns (-13%)
CdSe/CdS{Au}-2@ 510 nm	160 fs	10ps (-41%)	200 ps (-8%)	>1 ns (-51%)

8. Photodegradation Rate of Rhodamin Dye by The Core Shell, Au NP, Mixture of Au NP and Core Shell, HS 1 and HS-2.



SI Figure 8: Left panel: Absorption spectra of rhodamin B (RhB) dye in presence of (a) CdSe/CdS core shell (b) Mixture of Au and CdSe/CdS core shell, (c) HS 1 and (d) HS 2 at different time scale under 1 sun light illumination. **Right Panel:** Plot of C_t/C_0Vs time of RhB dye in presence of different materials under 1 sun light illumination.