Slow Electron Cooling Dynamics of Highly Luminescent CdS_xSe_{1-x} Alloy Quantum Dot

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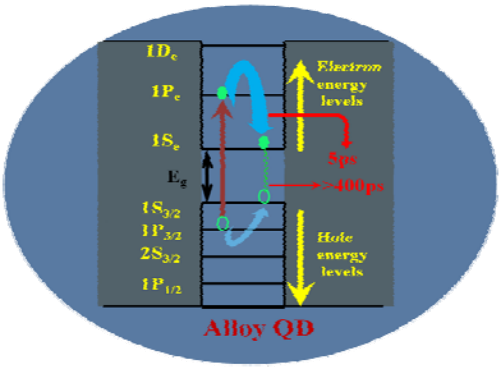
Abstract: Ultrafast Electron cooling dynamics of highly luminescent oleic acid caped CdS_xSe_{1-x} alloy quantum dot (QD) is investigated by femtosecond transient absorption studies and found to much smaller as compared to pure CdSe and CdS Qds.

Introduction: Alloy nanocrystals[1-2] quantum dots are important class of composite materials because of their enormous application like photovoltaic performances[3], coherent emitter, biological imaging, plasmon wave guide and magnetooptical devices etc. The physical and optical properties of the alloy semiconductor quantum dots depend on both size of the nanocrystals as well as the composition of the constituents and because of this, they play an extra degree of freedom towards selecting enviable properties for nanoscale designing purpose. The size dependent band structure of the semiconductor quantum dots appear due to their strong confinement regime which is governed by the size quantization effect (SQE). In case alloy quantum dots confinement of the charge carrier not only depend on size of the nanocrystal but it also varies on the constituent composition. Thus, by changing the composition of the constituents, one can achieve a next contrivance for altering physical and optical properties of the nanocrystal. For solar cell application it is very important to use quantum dot materials with very high luminescence yield, and longer exciton life time. It has been realized that higher efficient QD solar cell can be fabricated by using alloy nanocrystals. To obtain higher efficiency it is important to separate the electron and hole pair before the exciton annihilation takes place which occur in sub picoseconds time scale. Higher emission lifetime and emission quantum yield for alloy QD is reported, no literature is available on exciton cooling and recombination dynamics in ultrafast time scale for the same materials. In the present investigation $CdS_{0.3}Se_{0.7}$ alloy quantum dot has been synthesized after following high temperature synthetic method and characterized by using steady state optical and emission and time resolved luminescence spectroscopy techniques. Femtosecond transient absorption measurement has been carried out to understand hot carrier cooling dynamics and the charge carriers (electron-hole) recombination dynamics in ultrafast time scale.



***Scheme**. Carrier cooling/relaxation dynamics in alloy semiconductor quantum dot.*

Results and discussion:

Steady state optical absorption spectrum of the alloy QD shows an exciton absorption at 595 nm and the corresponding exciton emission appear sat 617 nm (figure1 left panel) which is shifted to red region of the spectrum as compared to

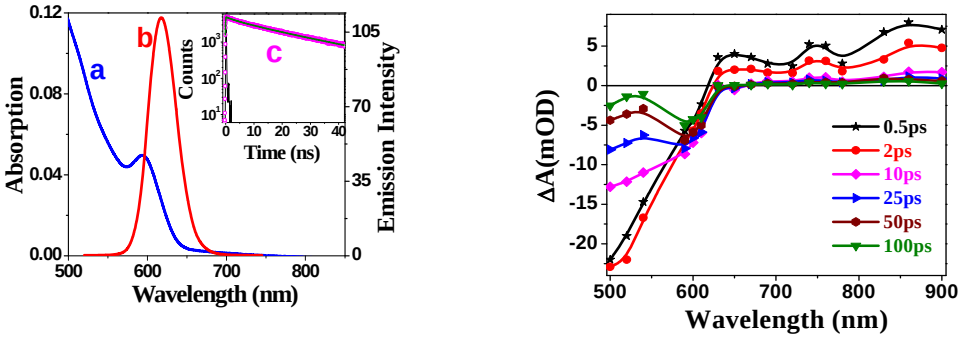


Figure 1: Left-Panel: Steady state (a) optical absorption and (b) emission spectra of $CdS_{0.3}Se_{0.7}$ alloy QD. **Inset:** (c) time resolved emission decay trace λ_{ex}=445nm and λ_{em}=617 nm. **Right panel:** Transient absorption spectra of that alloy recorded at different time delay following at 400 nm laser excitation.

that of pure CdS and CdSe QD with similar size. Emission quantum yield was determined to be ~ 70%. The high photoluminescence[4] of the alloy indicates that the electrons and holes are more confined in the nanocrystal. This is also confirm by slow time resolved fluorescence decay trace (inset left panel) measured at 617 nm after exciting 445 nm laser source and the emission trace can be fitted multi-exponentially with time constants τ_1 = 2.94 ns (13%) and τ_2 = 7.86 ns (5%) and τ_3= 21.37 ns (82%) with τ_{avg}=18.3 ns. Figure1 (right panel) depicts the transient absorption spectra of $CdS_{0.3}Se_{0.7}$ alloy QD which has bleach below 600 nm due to exciton absorption and a broad absorption from 650-900 nm can be attributed as trap state absorption of the charge carriers. To understand charge carrier dynamics the bleach recovery kinetics was monitored 500 nm (1P exciton, scheme 1) and 600 nm (1S exciton, scheme 1). Figure 2 shows that the comparison of bleach recovery and decay dynamics of alloy QD with pure material CdSe QD. The first excitonic (1S) bleach at 600 nm can be fitted with bi-exponential growth time constants τ_1= 100 fs (61%), τ_2= 5ps (39%) and multi-exponential recover time constants τ_1=120 ps (86%), τ_2>400 ps (14%) (Figure 2 trace a). On the other hand the upper excitonic bleach (1P, scheme) kinetics of the alloy at 500 nm (Figure 2 trace b) can be fitted with pulse-width limited growth (~100 fs) and bi-exponential recovery with time constant τ_1=14 ps (82%) and τ_2 = 100ps (18%). To compare charge carrier and recombination dynamics we have followed first excitonic (1S) beach recovery of CdSe QD and shown in Figure 2 c which can be fitted with 400 fs growth time. Finally the bleach recovers multi exponentially with time constants τ_1 = 5 ps (88%), τ_2 = 60 ps (29.4%) and τ_3 > 400 ps (-17.4%). Excitonic bleach of similar size CdS could not be measured as it appeared below 430 nm which is beyond the detection range of our spectrometer. The slow bleach recovery due to 1S for alloy QD can be attributed to electron cooling from upper exciton to first excitonic state which has been determined to be 5ps. The bleach recovery dynamics at 1S excitonic position is extremely slowed down in the alloy QD which indicates that the charge carriers become more confined in the QD. Our observation suggests that alloy QD materials can be used in solar cell applications due to very slow exciton cooling and also slower charge recombination.

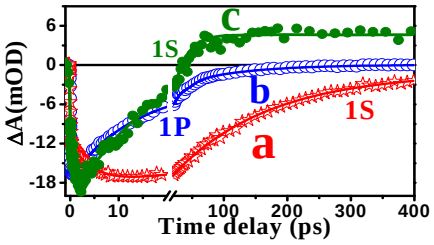


Figure 2: Bleach recovery dynamics of $CdS_{0.3}Se_{0.7}$ at two different wavelengths (a) 600 (1S) ,(b) 500 (1P) and (c) CdSe (1S) nm following at 400 nm laser excitation.

Conclusion:

In conclusion, we have synthesized $CdS_{0.3}Se_{0.7}$ quantum dot which has emission quantum yield as high as 70%. We are also reporting electron cooling time from upper excitonic state to lower excitonic state as slow as 5 ps for alloy $CdS_{0.3}Se_{0.7}$ quantum dot. In addition to carrier relaxation the charge carrier recombinations of the alloy QD also very slow which is also supported by very large emission quantum yield and long radiative life time. To the best of our knowledge we are reporting carrier cooling time of alloy ($CdS_{0.3}Se_{0.7}$) QD which is much slower as compared to pure CdS and CdSe QD materials.

References

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