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Unraveling the dual emission of single quantum-dot by single particle spectroscopy

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Abstract. Two-color emissive 0D–2D quantum-dot quantum-well (QD-QW) heteronanocrystals has created profound research activities. First multicolor emission in the visible region has been reported by Peng and co-workers in CdSe(core)–ZnS(barrier)-CdSe(shell) (core-barrier-shell) based heteronanostructures where the both CdSe phases (core and the shell) are emissive and tuneable as well. Owing to this enhanced and tuneable functionality, the QD-QW systems colloidal nanocrystals has fuelled their optical and imaging applications. Single particle spectroscopy has taken a giant step toward unravelling the features of individual particles and thus to provide direct information on their heterogeneity. To elucidate the dual emission characteristic of individual nanocrystals we performed energy mapped photoluminescence imaging. Surprisingly, the pseudo color PL intensity image shows that not all single particles are dual emissive in nature, few are either green emitting or red emitting. Photoluminescence spectrum of individual nanocrystals further confirms that individual nanocrystals can be dual emissive in nature. However, single color emissive dots are also present indicating the ensemble heterogeneity at single particle levels. The temporal evolution PL spectra of a single quantum shows spectral diffusion. The single dot experiments on the dual emissive QD-QW system unravels hidden photophysics which are otherwise not observed by ensemble spectroscopy.

1. Introduction

Low-dimensional materials such as quantum-dots,[1,2] quantum-rods,[3,4] core-shell quantum wells[5-7] have profound implications on the field of semiconductor physics, providing numerous fundamental observations as well as variety of optoelectronic applications. Owing to the quantum-confinement effect, the optical properties of the colloidal semiconductor nanocrystals are severely morphology dependent particularly when the particle radius is smaller than the exciton radius of the bulk material.[1,2] Over the past few years multi-quantum systems within a single nanocrystal, e.g., onion-like multiple thin shells surrounding the core, the supposedly quantum-dot-quantum-well (QD-QW) systems, have been explored. The first emergence of QD-QW systems in CdS core with an embedded layer of HgS (CdS/HgS) owing to research effort by Weller and co-workers.[5] Soon after, multi-quantum structures like (CdS)CdSe/CdS, (ZnS)CdS/ZnS (barrier-core) well-shell/barrier-shell, (CdSe)(ZnSe) (core-barrier)

etc. were flourishingly reported. Moreover, due to their enriching quantum information, few of these QD-QW systems were also able to seize attention for theoretical investigation.[8-10] However, all these early QD-QW hetero-nanostructures are mono color emissive. The rapid evolution of synthesis strategies for band gap modulation in core/shell heterostructures further resulted in so–called Dual Quantum System (DQS) hosting two distinct charge carrier recombination centres. In consequence, the corresponding photoluminescence spectrum are expected to display dual color photoluminescence emission bands should emanate from the spatially distinct radiative carrier recombination channels. Battaglia *et al.* developed an onion like quantum structure CdSe-ZnS-CdSe (core-barrier-shell) having two clear luminescent centres.[11] In this CdSe-ZnS-CdSe QD-QW structure, high band gap ZnS shell was sandwiched between two low band gap CdSe phases. This multi-color luminescence systems generated immense interests in photoluminescence imaging, biomedical labelling, molecular bar-coding,[12,13] light harvesting,[14] solid state lighting[15] because of the separation and localization charge carriers, markedly improved brightness, and enhanced color rendering index. This process of translational depends on comprehensive understanding of the photophysical dynamics of the building blocks, that is, individual luminescent quantum dots. Single particle spectroscopy has taken a giant stride toward unravelling the features of individual particles and thus to provide direct information on their heterogeneity.

In this work, we have performed photoluminescence imaging and spectroscopic measurements on CdSe(core)-ZnS(barrier)-CdSe(shell) nanocrystals at single particle level. Ensemble PL measurement shows dual emissive nature of these QD-QW systems, e.g., CdSe3ZnS4CdSe where the core emits in red (~625 nm) and the shell emits in yellow-orange (~575 nm) To elucidate the dual emission characteristic of individual nanocrystals we performed energy mapped photoluminescence imaging. Surprisingly, the false color PL intensity image shows that not all single particles are dual emissive in nature, few are either green emitting or red emitting. Photoluminescence spectrum of individual nanocrystals further confirms that individual nanocrystals can be dual emissive in nature. Intriguingly, single color emissive dots are also present indicating the ensemble heterogeneity at single particle levels. The red emission from individual QD-QW system can be assigned to exciton tunnelling through barrier ZnS layer to the core. However, only green emission originating CdSe shell is beyond our understanding. We have shown the temporal evolution PL spectra of a single quantum dot, clearly demonstrating spectral diffusion as the PL maxima are shifting. The preliminary single dot experiments on the dual emissive QD-QW system unravels hidden photophysics which are otherwise not observed by ensemble spectroscopy.

2. Experimental Methods

2.1 Synthesis of CdSe/3ZnS/nCdSe nanocrystals

For typical synthesis of CdSe, in a 50 mL three-necked round bottomed flask CdO (1 mmol), oleylammine (4 mmol) and octadecene (10 mL) were added and then heated to 260 °C with magnetic stirring under an argon atmosphere. Soon after the brown mixture turned into a transparent colorless solution, the temperature of the reaction vessel was dropped to 60 °C. Then 4 g octadecyl ammine and 2 g trioctylphosphine oxide were added to the solution and the temperature was set to reach 280 °C. When the solution temperature reached 280 °C, 1 mmol Se powder pre-dissolved in 4 mL trioctylphosphine solution was quickly inserted into the three-necked flask. To achieve the desired size of the nanocrystals, UV−vis absorption spectra was of the reaction solution was monitored and on achieving the targeted size of the NCs, the reaction was quenched quickly by removing the heating mantle and subsequently 10 mL toluene was added. Upon cooling down of the reaction mixture, 1:1 (v/v) hexane-methanol mixture was used to wash out the unreacted reagents. Acetone was used as non-solvent for precipitation of the NCs and toluene was used to redisperse the same. This process was repeated for 2-3 times. For synthesis of core-barrier-shell NCs, CdSe NCs of desired size and concentration (~1.44×10^{-4} mmol) were added to 2.5 g octadecylaminne and 5ml octadecene in a reaction vessel. The reaction mixture was evacuated and heated to 100 °C for at least 30 min. The reaction was then purged with Ar gas and the reaction was further heated to 200 °C. To grow the ZnS layers around the CdSe core, the S precursor was added first followed by the Zn precursor 20-25 min later. For this

particular investigation, three monolayers of ZnS were grown. For the growth of the CdSe shell on CdSe/ZnS NCs, the temperature was dropped from 200 °C to190 °C, and subsequently, Se and Cd precursors were added in the same fashion as in the case for the ZnS layers. Sufficient precursor was added for growth of only one monolayer at a time as per the method reported elsewhere.[16] One monolayer of ZnS and CdSe was approximated to be a 0.7 nm increase in diameter as estimated previously.[16] In a one-pot reaction both the ZnS and CdSe were coated on following similar strategy. After the final CdSe layer formation, the reaction mixture was again cooled to room temperature followed by the two times washing with a 1:1 hexane-methanol mixture for the removal of excess unreacted precursors. Either ethanol or acetone was used for the precipitation of the NCs and re-dispersion in toluene.

2.2 Single Particle Imaging and Spectroscopy
In order to obtain fluorescence microscopy image and spectrum with down to single particle resolution, a very dilute solution (~100 pM-1 nM) of QD-QW NCs in hexane was spin-cast in a polymethylmethacrylate (PMMA) matrix onto a freshly cleaned fused-silica substrate. At this concentration level, the NCs spacing are significantly larger than the diffraction limit of the microscope. A home-built wide field epifluorescence equipped with under 488 nm Ar ion laser (Mellos Griot) as excitation source was used for PL imaging and spectroscopy (Figure 1). In an inverted optical microscope (Nikon Eclipse 2000U) with epi-fluorescence mode, the 488 nm laser was used to excite the individual CdSe/ZnS NCs. For both the excitation and collection of fluorescence signal a 60X 1.49NA oil immersion objective lens (Nikon) was employed. In order to filter off the excitation beam light, a combination of dichroic mirror (Semrock – Di01-R488) and a 488 nm notch filter (NF03-488E-25) was deployed in the microscope filter cube turret. The fluorescence intensity image was recorded by air-cooled CCD camera (DVC-1412AM) at 100ms exposure times. In order to obtain dual-color image, two bandpass filters (Semrock): green-yellow (530-590 nm) and orange-red (590-700 nm) were used. Fluorescence emission intensity profiles of each discrete QD-QW NCs were recorded via a configuration of adjustable slit and transmission grating (70 grooves/mm, Optometrics) placed at an appropriate position in front of the CCD detector. This is to be noted that all microscopy data were obtained at the same excitation powers (~3-5 kW/cm^2) at 298 K. Due to small undulation in the excitation field, the single NCs fluorescence images were analysed after appropriate background subtraction. Using image analysis tool ImageJ (NIH), individual images of the exactly same area recorded in two different energetic channels (*i.e.*, green and red) were quantitatively superimposed to produce a false-color image. As a qualitative indicator, the 530-590 nm detection channel is assigned as green while 590-700 nm channel is red color. Once again, proper background adjustment and correction factor for detector response function were taken into account over the measured wavelength region.
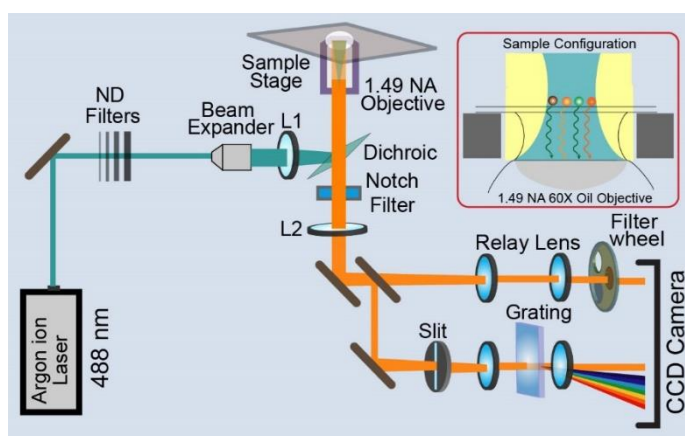

Figure 1. Homebuilt microscopy set up for single particle imaging and spectroscopy.

3. Result and Discussion

3.1. Ensemble Characterization of QD-QW Nanocrystals.

Certainly, the optical properties of nanocrystalline materials are unequivocally correlated to the extent exciton confinement, therefore, monitoring the absorption and emission characteristics have been sought out methods to gain insight into the electronic properties of NCs. The schematic of absorption—emission mechanisms of the core-barrier-shell based dual quantum system is shown in Figure 2a. The core CdSe is over coated with barrier ZnS shell having higher band gap than the CdSe. Further growth
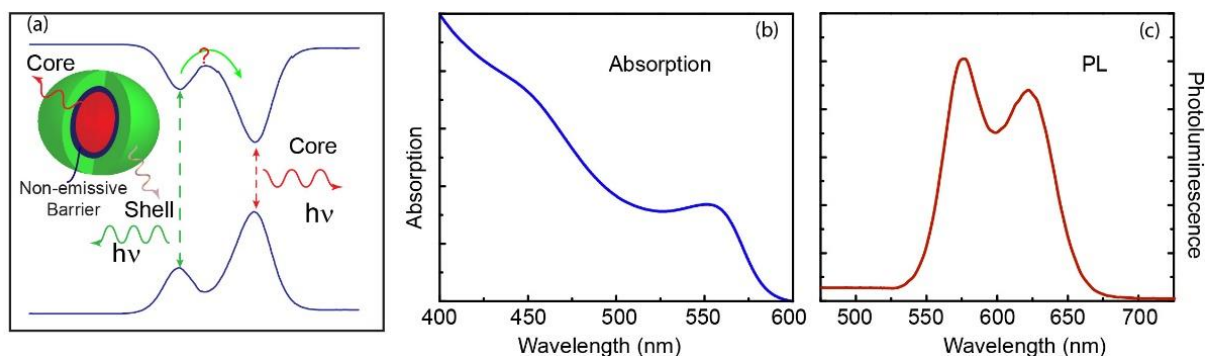

Figure 2. (a) Schematic of band structure of core-barrier-shell QD-QW nanocrystal and origin of dual PL emission of the sample under illumination. (b) Ensemble UV-vis absorption spectrum of CdSe/3ZnS/4CdSe NCs with clear dual excitonic band is displayed. (c) The ensemble photoluminescence spectrum shows dual emission bands with emission maxima at ~575 nm and ~620 nm.

of CdSe shell on the CdSe/ZnS enables the nanocrystal system as dual quantum system where core is assigned as QD and shell as QW. Figure 2b shows the optical absorption spectrum of core-shell nanocrystals. We have observed that there are two clear excitonic absorption peaks—one that appears at lower wavelength due to formation of CdSe shell while the longer wavelength excitonic peak emanates from the CdSe core. This observation is consistent with the size dependent confinement effect of semiconductor nanocrystals. The origin of dual emission from the onion like core-shell structure is shown schematically in Figure 2a. The ensemble photoluminescence spectrum of CdSe/3ZnS/4CdSe clearly demonstrate two distinct and sharp emission peaks (Figure 2c). This further corroborates with the two distinct exciton bands in the absorption spectrum. The photoluminescence band maximum at ~575 nm is originating from the 2D QW structure (CdSe shell) while 620 nm peak is assigned to the 0D
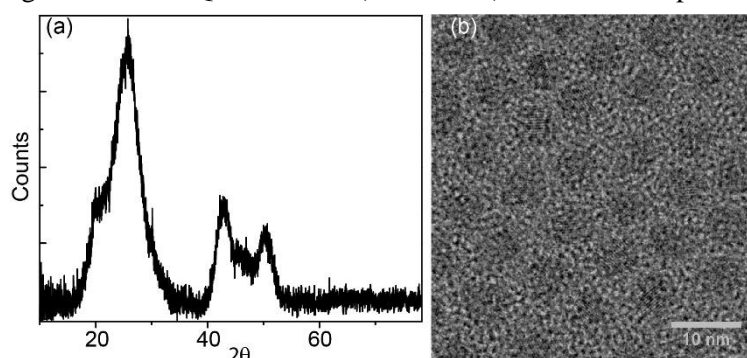

Figure 3. (a) Powder XRD pattern of CdSe/3ZnS/4CdSe nanocrystals showing zinc blend structure. (b) TEM image shows near-spherical structure of the NCs with nearly homogeneous particle size (scale bar -10 nm).

QD (CdSe core). The formation of the QD-QW structures stems from the structural characterizations. The powder X-ray diffraction (XRD) pattern is displayed in Figure 3a. In the x-ray diffraction pattern, the appearance of characteristic zinc blend reflections evidences the zinc blend nature of the QD-QW NCs. Figure 3b shows representative TEM image of CdSe/3ZnS/4CdSe structure attained by over-coating CdSe core with three monolayers of ZnS and subsequent four monolayers of CdSe. The QD-QW nanocrystals thus obtained are evidently spherical in nature. The NCs size distribution is nearly homogeneous with average particle size ~7.5 nm. The absence of any small particles further proves successful deposition of ZnS layers around the CdSe core and also the subsequent deposition of CdSe shells on CdSe/3ZnS. This also rules out the possible origin of dual emission band owing to the particle size distribution.

3.2. Single Particle Energy Mapped Imaging

Photoluminescence intensity image (12 μm × 12 μm) of QD-QW NCs acquired at 50 ms bin time and 3-5 kW/cm^2 excitation power is shown in Figure 4. The fluorescence imaging data very clearly demonstrate that individual luminescent spots are very bright with high signal-to-noise ratio. Moreover, almost all the luminescent spots show extensive fluorescence intermittency or blinking behaviours. Flickering of PL intensity or blinking of individual spots evidences that each luminescent spots are single particle in nature. Figure 4a shows the PL intensity image recorded in the energy channel 530-590 nm while Figure 4b in 590-700 nm channel for the same lateral area. Figure 4c is a resultant of the quantitative overlaying of Figure 4a and 4b. *Surprisingly*, as evident from Figure 4c that all the NCs are not necessarily dual emissive in nature. There are orange-yellow or greenish orange spots which are dual emissive in nature. This is consistent with the ensemble spectroscopy data where QD-QW emission shows dual peaks at ~575 nm and ~620 nm. Interestingly, exclusive red or green spots are also observed. These monocolour emissive centres originate either from CdSe core (red) or CdSe shell (green). The dual emission dots are consistent ensemble spectroscopic results. The question naturally arises whether single color emissive dots appear due to sample heterogeneity *i.e.*, inhomogeneous size-distribution of QD-QW NCs. However, the size-inhomogeneity can be ruled out directly from TEM image which clearly demonstrates near homogeneous size of the QD-QW NCs (Figure 3b). Single dot imaging provides ample qualitative evidence that not all NCs are dual emissive at single particle level. Therefore, further exploration of the luminescence photophysical dynamics warrants single particle spectroscopy for further quantification.
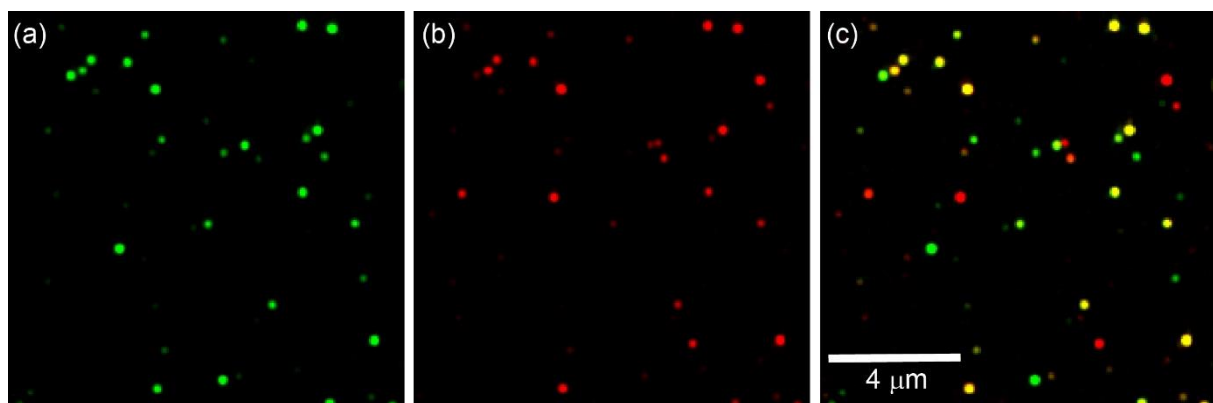

Figure 4. PL intensity images of CdSe3ZnS4CdSe QD-QW nanocrystals for a 12×12 micrometre area as obtained through (a) 530-590 nm (higher energy) band-pass filter, and b) 590-700 nm (lower energy) band-pass filter. The overlay of these two intensity images shown in (a) and (b) results in semi-quantitative pseudo-color energy-mapped intensity image (c). The variation of colours of individual emissive spots depicts single QD-QW are dual emissive as well as monocolour emissive.

3.3. Single Particle Spectroscopy of QD-QW NCs

Figure 5 (a) shows single particle PL spectra of seven representative QD-QW NCs. The PL spectrum of individual nanocrystal further approves that individual nanocrystal can be dual emissive (d1-4) in nature. These results also corroborate with the earlier study by Dias *et. al*.[14] Intriguingly, single color emissive dots are also present indicating the ensemble heterogeneity at single particle levels. The red emission from individual QD-QW system can be assigned to exciton tunneling through barrier ZnS layer to the core as schematically shown in Figure 2a. However, only green emission originating CdSe shell is hardly explainable. The only plausible mechanism may be due to large absorption section of the CdSe shell
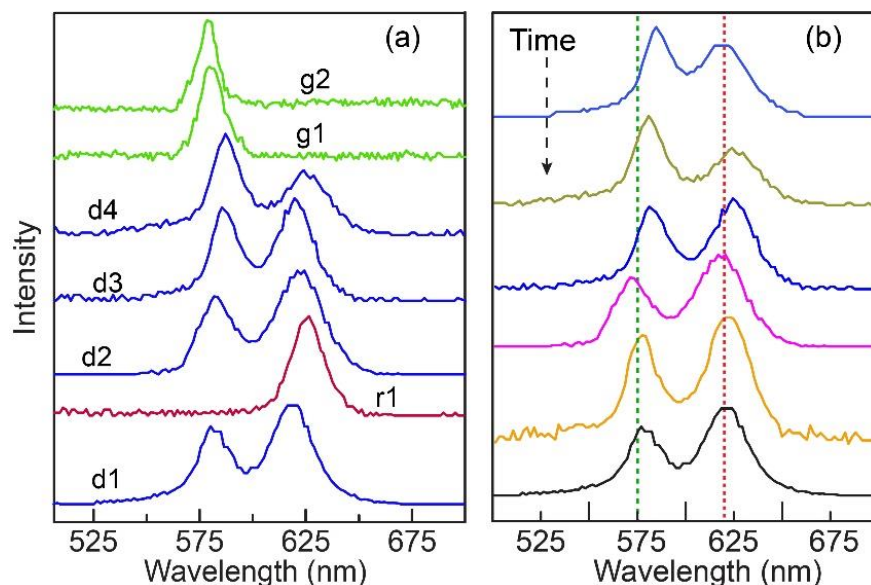

Figure 5. (a) Single particle PL spectra of seven representative QD-QW nanocrystals are shown. Individual dots show dual emission peaks (d1-4). Few dots also display single color emission peak either due to CdSe core (r1) or CdSe shell (green) (g1-2). (b) PL spectra of a single dual emissive QD-QW NCs at various times.

along with comprehensive localization of the exciton in the CdSe shell. Nonetheless, this requires further detailed investigation which is beyond the scope of this report. In the spectra of individual dots in Figure 5a, we observed that emission wavelength maxima of the dual color emissive dots (d1-4) are not appearing at the same energetic positions. This may be due the slight variation in the particle sizes. Moreover, we have also detected that the ratio of intensities of the dual two peaks are also fluctuating. The variation may be associated with fluorescence intermittency at single particle level. Further, there is possibility of variable exciton tunnelling rate from shell CdSe layer to core CdSe through the ZnS barrier. Therefore, among the dual emissive single dots there are substantial heterogeneity of the photophysical dynamic process. Therefore, to probe the exciton recombination dynamics and associated photophysics we have studied temporal evolution of PL spectra of a single quantum dot. In Figure 5b a typical PL emission traces at different time interval clearly demonstrate the shifting of emission peaks.

Fascinatingly, the PL intensity is also oscillating in the time series. This spectral diffusion can be attributed to the random trapping and detrapping of charges in the vicinity of the QD due to surface defects.[17-19] In colloidal NCs, spectral diffusion also has been attributed to the electric field undulations within the local NC environment which may induce a shift of the band edge spectra –popularly known as Stark effect.[20] Nevertheless, the actual reason for such spectral shift is a matter of further scientific research. Moreover, the line width of the PL emission spectrum at single particle level reveals narrower line-widths as compared to ensemble PL spectrum.

3.4. Single Particle PL Intermittency QD-QW NCs

The dual emissive phases of the QD-QW NCs provides the opportunity to investigate the cross-correlation for exciton tunnelling between the core and shell. Figure 6 depicts the single particle PL intensity trajectories, demonstrating the typical intermittency or blinking behaviour characteristic of a single particle. In the case of this dual emissive system, wavelength resolved PL intensity fluctuation is acquired with 200 ms binning time to distinguish whether both the phases are coupled or not. The intensity trajectories shown in Figure 6 both the CdSe core and CdSe shell trajectories show PL intermittency. This evidences single particle nature of the dual emitter. As depicted in this figure with double headed arrow indicates that decrease in PL intensity of the shell there is a concomitant increase in PL intensity of CdSe core. This correlated intensity fluctuation may be assigned as exciton tunnelling
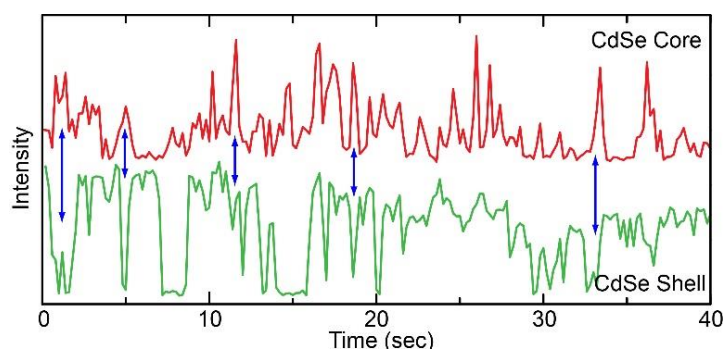

Figure 6. Wavelength resolved simultaneous PL intensity trajectory of core and shell emission.

from CdSe shell to CdSe core through the ZnS barrier. However, we find no measurable spectral diffusion at least on the 200 ms time scale of the experiment as the correlation of PL intermittency is inconsistent over the entire time trajectory. Therefore, brightening of PL emission of QD-QW structure due to CdSe shell growth over the CdSe/ZnS core is yet to be established at single particle level.

4. Conclusion

To summarize, fluorescence microscopy study on the CdSe3ZnS4CdSe QD-QW NCs at single particle level clearly displays new photophysical information which are obscured otherwise at ensemble level. The energy mapped imaging provides semi-qualitative information about emission behavior of individual particle which shows that all single particles are not necessarily dual emissive in nature. Single dot PL spectrum of individual nanocrystals confirms that individual nanocrystals can be dual emissive in nature. Intriguingly, single color emissive dots are also present indicating the heterogeneity in the exciton recombination dynamics at single particle levels. The fluctuating PL intensity and peak position also found to vary for individual dots. We have also shown the temporal evolution PL spectra of a single quantum dot clearly demonstrating spectral diffusion as the PL maxima are shifting. The preliminary results suggest that the core and shell may undergo spectral diffusion in non-synchronous fashion at least on the 200 ms bin time. The wavelength resolved time trajectories of 0-D CdSe core and 2-D CdSe shell displays uncorrelated flickering. Nonetheless, the preliminary single particle fluorescence study on the dual emissive QD-QW system unravels hidden photophysics which are otherwise not observed by ensemble spectroscopy.

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