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2019

Do, T. N., Zhang, C., Ong, X., Lian, J., Chan, Y., & Tan, H.-S. (2019). Measuring the Ultrafast Spectral Diffusion Dynamics of Colloidal CdSe Nanomaterials. *MRS Advances*, 4(1), 1–7.  
doi:10.1557/adv.2019.38

<https://hdl.handle.net/10356/144911>

<https://doi.org/10.1557/adv.2019.38>

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# Measuring the Ultrafast Spectral Diffusion Dynamics of Colloidal CdSe Nanomaterials

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*We use ultrafast coherent two-dimensional electronic spectroscopy (2DES) to study the ultrafast spectral diffusion dynamics of colloidal CdSe quantum dots (QDs) and CdSe nanoplatelets (NPLs). The Center Line Slope (CLS) and Nodal Line Slope (NLS) techniques were employed to analyse the 2DES spectra. We show that no spectral diffusion dynamics occurs for the CdSe QDs. On the other hand, spectral diffusion was observed in the CdSe 5 mono-layers NPLs heavy-hole transition. The normalized Frequency Fluctuation Correlation Function (FFCF) of the CdSe NPLs heavy-hole transition was measured to have a major fast decay component at 140 fs.*

## INTRODUCTION

One of the many challenges to the performances of nanomaterial-based applications such as biological imaging, solid state lightings and lasers, is the control of the ensemble emission linewidth [1]. This linewidth is usually assumed to compose of homogeneous and inhomogeneous contributions. The inhomogeneous linewidth is typically associated with the size distribution while the homogeneous condition is dictated by the spectral linewidths due to processes affecting individual particles such as phonon broadening [1-2].

In the context of the Kubo lineshape theory, we can consider the total lineshape of a material as the ensemble average of the time dependent transition frequency fluctuation that arises from the environment interactions [3]. In the Kubo lineshape theory, the timescale associated to the homogeneous linewidth is infinitely short as it can be thought of the individual transition instantaneously fluctuating over a frequency bandwidth. On the other hand, the inhomogeneous linewidth arises from static inhomogeneity and hence is infinitely long in timescale. This naturally introduces a regime

in between these two timescale extremes, which is due to fluctuation on the order of the timescale of the measurement. This is typically known as spectral diffusion. For nanomaterials, the processes happening in the femtosecond to picosecond timescale are very important, as it includes processes like hot excitons relaxation [4] and fast interplane exciton transport in nanoplatelets [5]. These processes affect the ultrafast spectral diffusion dynamics of the materials. Conversely, measuring the femtosecond to picosecond timescale spectral diffusion allows us an avenue to understand the microscopic details of these important processes.

Two-dimensional optical spectroscopy such as 2D Infrared (2DIR) spectroscopy and 2D electronic spectroscopy (2DES) has been routinely used to measure the femtosecond to nanosecond spectral diffusion dynamics of various molecular systems [6-8]. Here we report results of ultrafast spectral diffusion studies of colloidal CdSe quantum dots and nanoplatelets.

One of the key capabilities of 2DES is its ability to distinguish and quantify the homogeneous, inhomogeneous and spectral diffusion contributions to the spectral lineshapes of the measured system [9]. In 2DES measurements, three ultrashort visible light pulses interact with the sample. The interactions generate a third-order polarization in the sample which is then heterodyne-detected by a local oscillator pulse. The generated signal is mapped along the excitation and detection frequency axes, showing certain spectral shape and amplitude features. By carefully investigating the amplitude, peak position, lineshape, peakshape and dynamic evolution of the 2DES spectra, various information on molecular dynamics and structure can be revealed and determined in detail. Over the years, much effort has been spent on the analysis of the dynamics and peakshapes of the 2D spectra, both qualitatively and quantitatively. The simplest feature to measure is the diagonal width and the antidiagonal width of the peak describing a single transition, which give detail of the inhomogeneous and homogeneous linewidths, respectively [9-10]. This principle is being used by a recent work by Turner et al., which studied the size dependence of CdSe QDs' homogeneous linewidths. They observe that the homogeneous linewidth decreases as QD radius increases, by characterizing the antidiagonal peakwidths of band-edge 2DES spectra (representing the  $1S_{3/2}-1S_e$  transition). They observe that the homogeneous linewidth decreases as the QD radius increases [11].

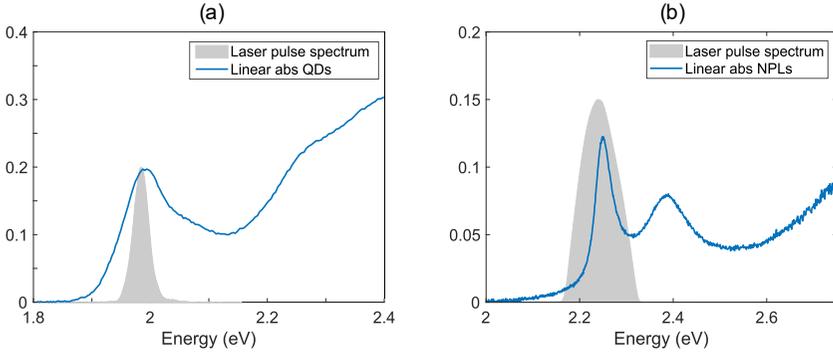
An important quantity that characterizes homogeneity, inhomogeneity and spectral diffusion is the frequency-fluctuation correlation function (FFCF) [9]. A variety of methods can be utilised to retrieve the FFCF from a 2DES experiment. These methods include the central line slope (CLS) [12-13], ellipticity [14-15] and eccentricity [16] methods. All the above methods have been shown to be linearly proportional to the FFCF under certain assumptions and limitations. Another related technique to recover information on the homogeneity, inhomogeneity and spectral diffusion of a system is the nodal line slope (NLS) analysis [17]. This technique takes advantage of the interference of positive value bands and negative value bands in 2D spectra.

In the following section, we will report on the use of NLS and CLS analyses, to study the spectral diffusion dynamics of colloidal CdSe quantum dots and nanoplatelet, respectively.

## EXPERIMENTAL

Spherical monodispersed wurtzite CdSe QDs were synthesized and processed according to protocols previously reported by Chakraborty et al. [18], which yields nanoparticles with band-edge absorption at 1.984 eV. The CdSe QDs have an average diameter of 4.9 nm and a size distribution of about 11%.

Five mono-layer (5ML) colloidal CdSe NPLs were prepared according to protocols previously reported by Guzelturk et al. [19]. The 5ML CdSe NPLs has peaks at 2.25 eV and 2.38 eV corresponding to the heavy-hole (HH) and light-hole (LH) transitions.

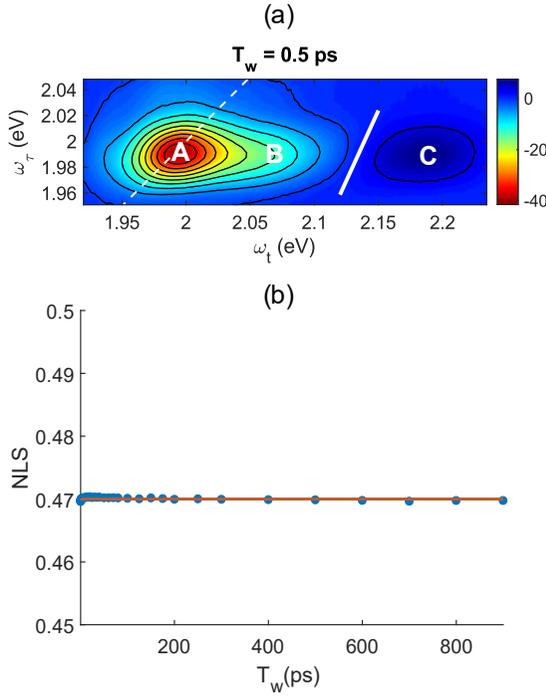


**Figure 1.** (a) Linear absorption spectrum of the CdSe QDs overlaid with the corresponding excitation pulse spectrum. (b) Linear absorption spectrum of the CdSe NPLs overlaid with the corresponding excitation pulse spectrum.

The 2DES measurements are carried out on a 2D electronic spectrometer based on a pulse shaper assisted pump probe geometry which was previously described in Ref. [20]. Briefly, a commercial Ti:sapphire crystal amplified laser system (Legend Elite, Coherence) with an output pulse centered at 800 nm was used to pump a home-built, double-stage optical parametric amplifier and second harmonic generator, to produce pump pulses tunable in the visible regime. For the experiments reported here, the pulses were tuned to 625 nm (1.98 eV) to coincide with the band-edge  $1S_{3/2}-1S_e$  ( $X_1$ ) transition of the CdSe QDs (Fig. 1(a)) and to 550 nm (2.25 eV) to coincide with the heavy-hole (HH) transition of 5ML CdSe nanoplatelets (Fig. 1(b)). The single pump pulse is passed through an acousto-optic programmable pulse shaping unit (Dazzler, Fastlite) to create a double-pulse train with controllable time delay  $\tau$ . These pump pulses have a pulse duration of 57 fs with 2 nJ energy per pulse. The probe light is a white light continuum pulse created by focusing a small portion of the 800 nm fundamental pulse onto a sapphire window. The probe pulse is then detected at waiting (or pump probe delay) time  $T_w$  after the double-pulse pump. The transient absorption spectra of the probe pulse is then measured as a function of  $\tau$  as  $S(\omega_t, T_w, \tau)$  where  $\omega_t$  is the probe pulse detection axis. Finally,  $S(\omega_t, T_w, \tau)$  is then Fourier transformed over  $\tau$  and processed to give the 2DES spectra  $S_{2D}(\omega_t, T_w, \omega_\tau)$ .

## RESULTS AND DISCUSSIONS

### CdSe Quantum dots



**Figure 2.** (a) The 2DES spectrum at  $T_w = 500$  fs of CdSe QDs. The white dotted line is the diagonal. The white solid line depicts the nodal line separating features B and C. (b) The NLS values (dots) vs.  $T_w$  from 300 fs to 900 ps overlaid with a fitted line which correspond to a constant value of 0.47 (solid line).

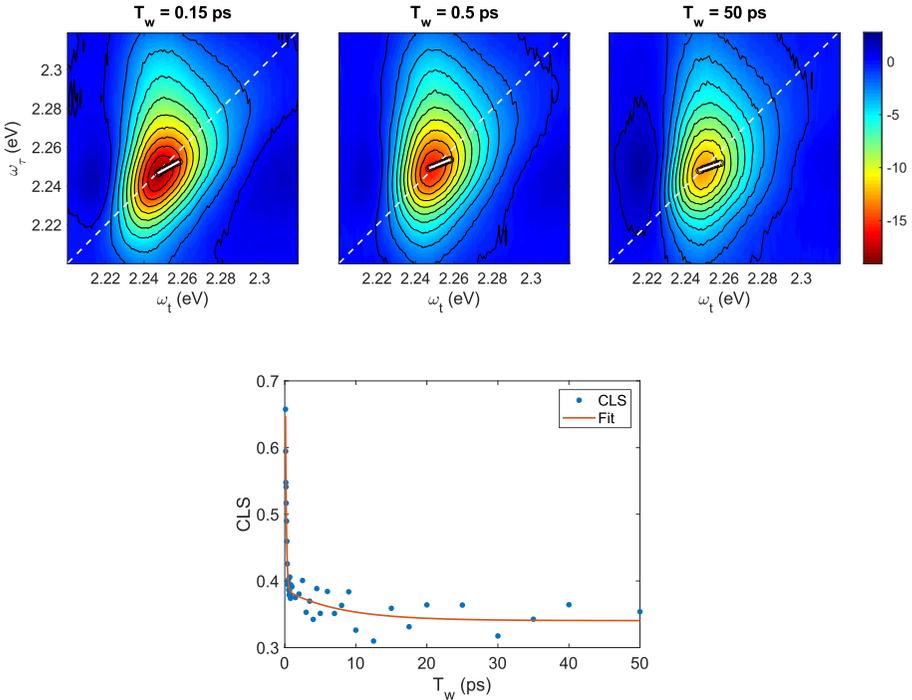
A 2DES spectrum at  $T_w = 500$  fs is depicted in Fig. 2(a). The features of the spectra have been explained in a recent publication [21]. There is one negative diagonal peak in the 2DES spectrum (feature A in Fig. 2(a)). It arises from the  $X_1$  transition. As viewed along the probe dimension, there is a negative cross peak (feature B in Fig. 2(a)) associated with the  $(2S_{3/2}-1S_e)$   $X_2$  transition. Due to broadening effects, especially at room temperature, this cross peak is not well resolved and appears as a spread from the diagonal peak along the probe axis. Further away from the diagonal peak, the positive cross peak (feature C in Fig. 2(a)) arises from the redshifted ESA of the  $X_3$  ( $1P_{3/2}-1P_e$ ) transition. These peak positions agree with the results and assignment from TA spectrum [22].

We define NLS as the inverse of the slope of the nodal line, which connects the nodal points of the horizontal slices of the 2DES spectrum. Since the  $X_1$ ,  $X_2$  and  $X_3$  states are overlapped to a certain extent in the spectral domain and the biexciton binding energy shift is small [23], especially for the  $X_1$  state (a few meV), the positive peaks corresponding to  $X_1$  and  $X_2$  ESA processes were sufficiently offset by the dominance of the negative signals, thus rendering them unobserved. As a result, the apparent NLS shows up only in the position between the  $X_2$  negative peak and the  $X_3$  positive peak and the NLS analysis was conducted on this line. Each one-dimensional cut through the 2DES spectrum, which is parallel to the probe axis, is fitted using a polynomial function so that accurate nodal points can be determined. The resulting nodal points can be fitted linearly within the pump

excitation region. The solid white line in Fig. 2(a) shows the resulting nodal line fit from the experimental data in the vicinity of the pump maximum as an example. In principle, the NLS value varies from 0 to 1. The inhomogeneity, homogeneity and spectral diffusion of the transitions that give rise to features A, B and C determine the specific value of NLS at any given waiting time  $T_w$  [21].

From the experimental data in Fig. 2(a) at  $T_w = 500$  fs, we measure the NLS value to be 0.47. Figure 2(b) depicts the measured NLS value versus the population time  $T_w$ . It can be seen that the data points tend to follow a constant value of 0.47 over the observation window of 0.3 to 900 ps. This behavior shows that there exists negligible spectral diffusion over the time scale of our measurements. This indicates that the lineshape of the CdSe QDs can be adequately described as involving only inhomogeneous and homogeneous contributions. Our observation is consistent with what was observed by Turner and co-workers, where 2DES was performed for colloidal CdSe QDs of sizes ranging from 1.7 nm to 3.0 nm [24]. In the resultant data, the antidiagonal and diagonal width of the peak assigned to the band-edge  $1S_{3/2}-1S_e$  ( $X_1$ ) transition remains constant for  $T_w = 75$  fs to 900 ps, thus showing a lack of spectral diffusion over these timescales.

### CdSe Nanoplatelets



**Figure 3.** (Top) Representative 2DES spectra of the heavy-hole transition of CdSe NPLs at  $T_w = 150$  fs, 500 fs and 50 ps. The central lines are depicted as the white solid line. (Bottom) The CLS values vs.  $T_w$  from 150 fs to 50 ps (dots) overlaid with a fit of a sum of three exponential functions (solid curve).

2DES spectra of the HH transition of 5ML CdSe NPLs at waiting time  $T_w = 150$  fs, 500 fs and 50 ps are presented in Fig. 3. It is clear that there is a  $T_w$  dependent variation in the 2DES peakshape, with a more elongated shape at shorter  $T_w$  to a more rounded shape at longer  $T_w$ . This indicates that the HH transition undergoes spectral diffusion over the timescale of the experiment. As the peak is clearly separated and there is minimal

interference from other transitions, the CLS technique [12-13] can be used to analyze and recover the normalized FFCF  $\bar{C}(T_w)$ . We take slices of the 2DES spectrum parallel to the pump frequency axis  $\omega_\tau$  and determine the maximum signal position for the slice. Collected in such way, the series of peak positions were then fitted by linear regression, from which the gradient is defined as CLS. The fitted CLS from the corresponding 2D spectrum is denoted by the white solid line superimposed onto the plot. The gradient at different values of  $T_w$  gives  $\bar{C}(T_w)$  [25]. The bottom graph of Fig. 3 shows the recovered the measured  $\bar{C}(T_w)$  value from  $T_w = 150$  fs to 150 ps. Note that in the Fig. 3, we only present data up to  $T_w = 50$  ps to show the fast decay in a clearer manner. The measured  $\bar{C}(T_w)$  can be fitted with three exponential decays with amplitudes  $A_i$  and decay constant  $\tau_{c_i}$  (solid line in the bottom graph of Fig. 3). The summary of the CLS fitting results is presented in Table 1. Theoretically,  $\bar{C}(T_w)$  can bear a value of 1 at  $T_w = 0$ . In our current data, the amplitudes add up to 0.93. As our shortest  $T_w$  value is 150 fs, it is likely that there is a fast component of <100 fs that our experiment cannot resolve. We may view this as a homogeneous component. In our measured data, the major component of decay is  $A_1$  with a timescale of 140 fs. There is a slower and more minor spectral diffusion component ( $A_2$ ) at a longer timescale of 7.7 ps. The last component with an amplitude  $A_3$  of 0.34 can be attributed to the inhomogeneous contribution to linewidth.

**TABLE 1. CLS FITTING RESULTS OF CdSe NPLs**

| <b>i</b>                            | <b>1</b>            | <b>2</b>             | <b>3</b>            |
|-------------------------------------|---------------------|----------------------|---------------------|
| <b><math>A_i</math></b>             | 0.54 ( $\pm 0.07$ ) | 0.047 ( $\pm 0.01$ ) | 0.34 ( $\pm 0.01$ ) |
| <b><math>\tau_{c_i}</math> (ps)</b> | 0.14 ( $\pm 0.02$ ) | 7.7 ( $\pm 4.3$ )    | >>1 ns              |

Identifying and understanding the microscopic processes that results in the fluctuation in the HH transition frequency, represented by  $A_1$  and  $A_2$  will be important in a better understanding of the photophysics of CdSe NPLs.

Based on the observations that there is no measurable spectral diffusion in the zero-dimensional QDs while spectral diffusion was measured in the two-dimensional NPLs, we may be able to speculate about the physical origin of the spectral diffusion observed in the NPLs. The spectral diffusion may have arisen from the excitons moving and sampling different locations on the NPLs plane. In the process, the heterogeneity and unevenness of the NPLs plane causes the fluctuation in transition frequency of the excitons.

## CONCLUSIONS

We performed 2DES measurements on colloidal CdSe quantum dots and CdSe 5 ML nanoplatelets. We measure the ultrafast spectral diffusion dynamics of the  $1S_{3/2}-1S_e$  transition of QD and the heavy-hole transition of the NPLs. In QDs, we observe no spectral diffusion from 300 fs to 900 ps. The conventional analysis of the spectrum of QDs to comprise of only homogeneous and inhomogeneous contributions is valid. On the other hand, we measure a significant ultrafast spectral diffusion component of 140 fs timescale in the CdSe NPLs. This implies that there is some process of that timescale that is causing the fluctuation of the transition frequency. Identifying this process will be important to achieve a thorough understanding of this type of nanomaterial.

## ACKNOWLEDGEMENTS

This work is supported by a grant from the Singapore Ministry of Education Tier 2 Academic Research Fund (MOE2015-T2-1-039).

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