

Rate Dispersion in the Biexciton Decay of CdSe/ZnS Nanoparticles from Multiple Population-Period Transient Spectroscopy

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S Supporting Information

ABSTRACT: Measurements of biexciton decays in semiconductor nanoparticles are easily contaminated by contributions from photoproducts or higher excitons. Theoretical work has shown that multiple population-period transient spectroscopy (MUPPETS) can measure biexciton decays free from these interferences. In this communication, the biexciton decay of CdSe/ZnS core-shell nanoparticles is measured with MUPPETS. The decay is strongly dispersed (nonexponential) with a more than 5-fold range of rates. This large dispersion must be accounted for in the decay mechanism and in the measurement of biexciton dynamics by more conventional methods. The success of MUPPETS in this context lays the foundation for using it to study exciton–exciton interactions in a variety of materials.

The lifetime of a biexciton is important in many optoelectronic applications of semiconductor nanostructures.^{1–3} Early on, Auger recombination was identified as a likely decay mechanism.^{4,5} Properties of the core were seen as primary in controlling the rate. As a one-step relaxation, it should have an exponential decay on a single particle, and as a core-based mechanism, it should have a relatively uniform rate from particle to particle. Thus, the ensemble biexciton decay has often been assumed to be exponential. Observations of nonexponential decay are easily attributed to additional contributions from higher multiexcitons or photoproducts. In this communication, a six-pulse, multidimensional spectroscopy is used to separate the biexciton decay from other potential contributions. The biexciton decay is found to be highly dispersed, i.e., nonexponential, and the form of the rate dispersion is accurately measured.

In many experiments on semiconductor nanoparticles, excitons, biexcitons, and higher multiexcitons are created simultaneously. Isolating the biexciton contribution is not simple. The separation between exciton and biexciton transitions is small, making their spectral resolution difficult.⁶ Analyzing the fluence dependence is complicated by saturation combined with spatial variation of the light intensity within the sample.

Because of these problems, the identification of biexcitons and the quantification of their properties have often relied on the decomposition of kinetic traces into exponential components.^{4,5,7–9} Slow, fluence-independent components are identified as excitons, and fast, fluence-dependent components are identified as multiexcitons. The assumption of exponential

decay has been explicitly used to decompose the faster, fluence-dependent component into bi-, tri-, and higher excitons.^{4,7} This approach has been widely used to study the biexciton decay mechanism⁵ and to identify multiple exciton generation from single photons.^{8,9}

However, recent investigations make the form of the biexciton decay less certain and change it into an important experimental question. Challenges to the Auger mechanism have been raised,^{10–12} opening the possibility of a multistep mechanism and/or a mechanism with greater particle-to-particle variation. Even within the Auger model, an important role for the surface is being recognized.¹³ Bawendi and co-workers have argued that surface heterogeneity can translate into a distribution of biexciton decay rates.¹⁴ Single-particle experiments have found particle-to-particle variation in the biexciton quantum yields that support this idea.^{14,15}

It has also been appreciated that long-lived, but reversible, photoproducts can mimic biexcitons in a kinetic analysis.^{3,8,16} Various experiments, single-particle blinking,^{2,17} transient absorption,¹⁸ and photobleaching,¹⁹ suggest the existence of one or more photoproducts with a low quantum yield of emission, i.e., with a fast exciton lifetime. A charged particle is a leading candidate for such a photoproduct, but the topic is still unresolved. The photostationary concentration of a photoproduct scales with the excitation fluence, just as the biexciton concentration does, and the photoproduct exciton has a fast decay, just as the biexciton does. If such a photoproduct contaminates a measurement, a multiexponential decay could be falsely attributed to the biexciton.

We use multiple population-period transient spectroscopy (MUPPETS) to measure the form of the biexciton decay in CdSe/ZnS core-shell nanoparticles free from these complications. MUPPETS is a 2D form of ultrafast kinetics: two excitation pulses are separated by a time t_1 , and the change in absorbance due to both excitations $A^{(2)}(t_2, t_1)$ is measured after an additional time t_2 .²⁰ The phase-matching condition creates a double difference between the four possibilities of absorption or no absorption from each of the two excitations. The resulting signal isolates the effects due to an interaction between the two excitations. To create the required phase-matching condition, each of the excitations and the final measurement consists of two simultaneous pulses entering the sample from different directions. Thus, the experiment uses a total of six pulses and measures an incoherent component of the $\chi^{(5)}$ response of the sample.

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Previously, MUPPETS has been used in systems with only two electronic levels, where it measures heterogeneity in the rate of the electronic decay.²⁰ A recent theoretical analysis has revealed a new feature of MUPPETS in multilevel systems—the ability to discriminate between biexcitons and photoproduct excitons.²¹ In pump–probe and other one-dimensional experiments, the signals from excitons and biexcitons have the same sign, but in MUPPETS they have opposite signs. Starting from the ground state, the first excitation always creates an exciton and reduces the band-edge absorption by approximately one-half. The second excitation has two possibilities. In one pathway, a biexciton is created, reducing the band-edge absorption to zero. In our sign convention, this increased bleach is negative. In the other pathway, the second excitation again creates excitons from ground-state particles, also bleaching the total absorption. However, due to the initial depletion of the ground state by the first pulse, the second pulse has a reduced effect. The effect unique to combining the two excitations is a smaller bleach, which has a positive signal in our sign convention.

Consider a sample with normal particles, which have a slow exciton and a fast biexciton decay, and a fluence-dependent, steady-state concentration of a photoproduct, in which both exciton and biexciton decays are fast. In the low fluence limit, a $\chi^{(3)}$ pump–probe experiment measures only the slow exciton decay of the normal particles. The first-order fluence dependence is a $\chi^{(5)}$ term that contains the fast biexciton decay of the normal particles and the fast exciton decay of the photoproduct, both with the same sign. As a $\chi^{(5)}$ experiment, MUPPETS contains all these contributions, even in the low fluence limit. However, the normal and photoproduct excitons both give a positive signal, whereas the normal biexciton gives a negative signal. This sign change allows the normal biexciton to be distinguished from a potential photoproduct.

Huxter and Scholes previously used a related $\chi^{(5)}$ experiment to study biexciton dynamics,²² but this communication is the first to demonstrate and exploit the sign difference of exciton and biexciton signals. The separation of exciton and biexciton signals requires only the $t_1 = 0$ cut through the MUPPETS data. The additional information available from the full 2D data set will be analyzed in a future paper.²³

The samples were commercial (NN-Labs) CdSe/ZnS core–shell nanoparticles in toluene with an OD of 0.4 in the 1 mm sample cuvette at the band-edge absorption peak of 520 nm. To reduce the concentration of photoproducts, the sample was flowed through the cuvette with a peristaltic pump and was kept under a nitrogen atmosphere. Excitation fluences are reported as the energy per pulse at the sample in an $\sim 200 \mu\text{m}$ diameter spot size. All the pulses had the same wavelength (527 nm), which is near the band edge. Pulse widths were ~ 300 fs, but results are only reported after 1 ps, when fine-structure relaxation is complete.²⁴ The details of the instrument are reported elsewhere.²⁰

Fluence dependent pump–probe experiments are reported in Figure 1A. This method is conventional for measuring biexciton yields and dynamics.⁵ The data have been normalized at long times, when only the exciton remains. The early, fluence-dependent decay component may be due to biexcitons or photoproduct excitons. Higher multiexcitons also create absorbance at the band edge, although the mechanism is not well understood.^{4,7} With excitation at the band edge, we hope to avoid creating higher multiexcitons in the first place. The underlying fluence-independent component is assigned to the

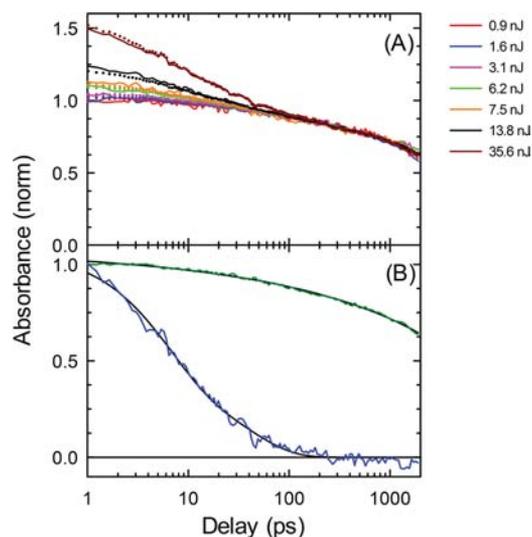


Figure 1. Fluence-dependent, band-edge pump–probe results. (A) Solid: decays at various pulse energies normalized to match at long times. (An additional four energies are shown in Figure S2.) Dots: data reconstructed from the results in (B). (B) Linear regression at each time point reduces the data of (A) to two components: a low-fluence limit (intercepts, green) and a linear, fluence-dependent component (slopes, blue). The fluence-dependent component is fit to two exponentials (black). Other possible fits are shown in Figure S1. The fit to the fluence-independent component (black) shows rate dispersion in the exciton as well.²³

exciton. The exciton not only has a strong radiative decay component near 20 ns but also has decay components throughout the picosecond range.⁹ The rate dispersion in the exciton decay will be discussed in a future paper.²³

To avoid any assumptions about the form of either the exciton or biexciton decay, the data have been analyzed by linear regression at each time point. The intercepts (green, Figure 1B) form the fluence-independent (exciton) decay; the slopes (blue, Figure 1B) form the fluence-dependent (biexciton/photoproduct) decay. The linearity of the fluence dependence was verified by reconstructing all 11 of the original data sets from these two components (dots, Figure 1A) and verifying that there is no systematic deviation.

The fluence-dependent component is distinctly nonexponential. This rate dispersion could be attributed to inadvertent creation of a triexciton. A 3-fold ratio of biexciton to triexciton rates has been reported.⁷ This ratio is roughly consistent with the data, although the use of band-edge excitation and the linearity of the fluence dependence both argue against this interpretation. Alternatively, the dispersion could be attributed to accumulation of a photoproduct. The decay rate of the most likely photoproduct, a charged particle, is predicted to have a 4-fold ratio with the biexciton rate.²⁵ Again, this ratio is roughly consistent with the data, but the use of a flowing sample argues against this interpretation. Finally, the dispersion could be inherent to the biexciton itself, despite the lack of a mechanistic justification.

The difficulties in interpreting the pump–probe results are resolved by the MUPPETS data in Figure 2. The MUPPETS data have been recorded as a function of fluence and extrapolated to the low fluence limit, as the pump–probe data were.²³ This procedure eliminates potential photoproduct biexcitons, which might contribute at higher fluences. The magnitude of the complex signal at $t_1 = 0$ is given as the red

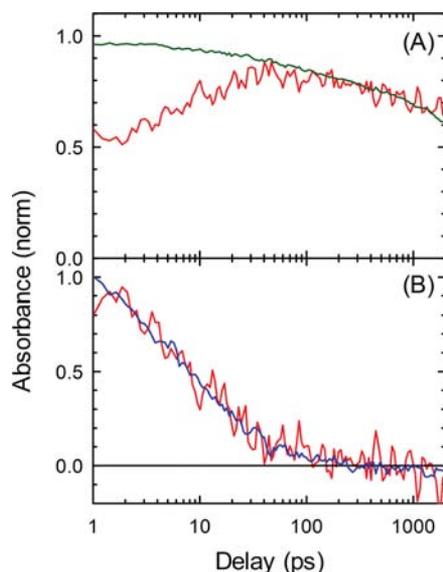


Figure 2. (A) Magnitude of the MUPPETS absorbance $A^{(2)}(t_2, t_1)$ vs t_2 at $t_1 = 0$ (red) and the fluence-independent component from pump–probe measurements (green, from Figure 1B). (B) The difference between the curves in (A) gives the biexciton decay (red). It is identical to the fluence-dependent component of the pump–probe measurements (blue, from Figure 1B).

curve in Figure 2A. These data are the sum of a positive exciton signal and a negative biexciton signal. As the negative biexciton contribution decays, the net signal rises. This rise confirms the theoretical prediction in ref 21 of opposite signs for the exciton and biexciton signals. The initial value of 0.5 is consistent with the exciton-to-biexciton cross section being one-half the ground-to-exciton cross section,²³ as predicted by simple, one-electron models.⁵

The biexciton decay is isolated by matching fluence-independent (exciton) data from the pump–probe experiment (green, Figure 2A) at long times and subtracting the MUPPETS data (red, Figure 2A) from them. The result is the red curve in Figure 2B. Because this result is derived from data in the low fluence limit, it is free of higher multiexcitons. It is compared to the fluence-dependent decay from pump–probe measurements (blue, Figure 2B), which may contain contributions from a photoproduct. No modeling or fitting of the data is involved in this comparison.

The biexciton decay found from MUPPETS is identical to the fluence-dependent component of the pump–probe measurements. This agreement is direct evidence that the precautions taken to eliminate other contributions to the pump–probe experiment have been sufficient and that the rate dispersion is intrinsic to the biexciton decay. The degree of rate dispersion is large enough that it must be accounted for in the decomposition of multiexciton decays. It also demands a revision or extension of the biexciton decay mechanism that can account for the dispersion.

Quantifying the rate dispersion depends on the mechanism assumed. The dispersion could be due to (1) a multistep relaxation of the biexciton, (2) a relaxation in the environment (e.g., movement of surface species) that causes the decay rate to slow as a function of time and is initiated by the creation of an exciton or biexciton, or (3) a distribution of rates among the particles. A biexponential fit (Figures 1B and 3), which is consistent with mechanism (1), gives a 7-fold ratio of rates.

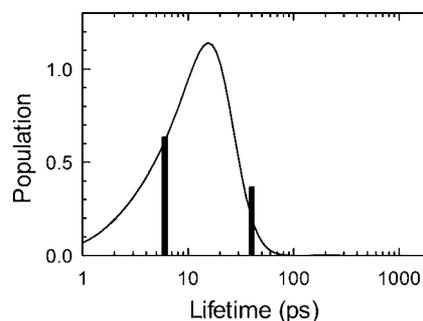


Figure 3. Lifetime distributions of the biexciton decay. The bars represent a biexponential fit. The solid curve is a continuous distribution from a maximum entropy fit. For other possible fits, see SI.

Assuming a time-dependent rate, which is consistent with mechanism (2), gives a 25% drop in rate in 40 ps. A fit to a continuous distribution of rates, which is consistent with mechanism (3), gives a distribution with a 5-fold range of rates at the half-width of the distribution (Figure 3). A stretched exponential, which is often used to describe complex dynamics, gives a stretching parameter of $\beta = 0.5$. Regardless of the description used, the rate dispersion is substantial. (More details on the various fits are given in the Supporting Information, SI.)

The biexciton decay rate is known to depend on the particle radius,⁵ but simple size heterogeneity cannot cause the observed rate dispersion. A 5-fold variation in rate would require a 1.7-fold variation in radius. This variation would also cause a range of 160 nm in the band-edge position,²⁶ which is not observed spectroscopically. Thus, mechanism (3) requires surface heterogeneity that affects the biexciton decay.

Nair et al. have recently shown that single particle (SP) photon-correlation measurements yield the ratio of biexciton-to-exciton quantum yields.¹⁴ Using this method, Park et al. reported a 4-fold spread in biexciton quantum yields from particle-to-particle but in a rather different system, CdSe with a thick CdS shell.¹⁵ Nair et al.'s measurements on CdSe/CdZnS nanoparticles also showed particle-to-particle variation in the biexciton quantum yields but with less than a factor of 2 variation.¹⁴ These results suggest that heterogeneity accounts for part of the rate dispersion seen here but might not account for all of it.

Several differences between SP measurements and MUPPETS may account for the apparent difference in results. First, SP measurements average over ~ 100 s of data collection time.¹⁴ If a heterogeneity fluctuates during this time, it will be seen by MUPPETS but not by SP measurements. Second, a homogeneous source of rate dispersion, such as mechanisms (1) or (2), would not be evident in the SP quantum yield. Third, although both techniques seek the limit of low peak powers, the average powers differ by three orders of magnitude: 30 W/cm² on a static sample for SP measurements and 0.030 W/cm² on a flowing sample for MUPPETS measurements. Thus, the issues presented by photoproducts can be quite different in the two experiments.

The results in this work confirm the recent theoretical treatment of MUPPETS in a general excitonic system²¹ and indicate the potential for similar applications of MUPPETS to many other such systems. The biexciton decay measured here is analogous to exciton–exciton annihilation in conjugated polymers, quantum wells, dye aggregates, and photosynthetic

systems. MUPPETS has the potential to contribute to understanding exciton transport and exciton–exciton interactions in all such systems.

■ ASSOCIATED CONTENT

📄 Supporting Information

Parameters and plots of various fits to the biexciton decay and additional data not shown in Figure 1A. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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