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Article

Sample Concentration Affects Optical Gain Results in Colloidal Nanomaterials: Circumventing the Distortions by Below Band Gap Excitation

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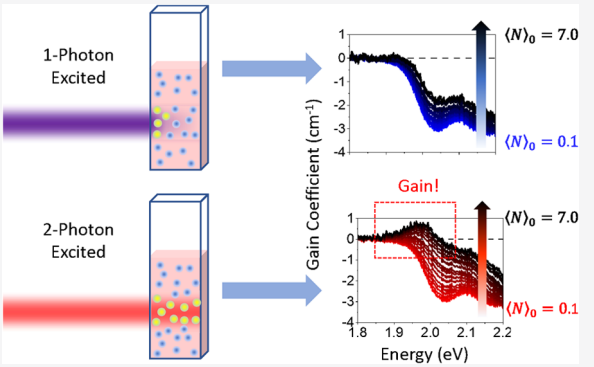
ABSTRACT: Ultrafast spectroscopy studies have been key to the development of optical materials, including colloidal semiconductor nanocrystals (NCs) engineered for lighting and light-harvesting technologies. Several physical processes, which are revealed by ultrafast spectroscopy in NCs, are highly dependent on the average number of excitons created per NC, including optical gain properties and multiexciton interactions. Consequently, proper considerations regarding NC populations are necessary to avoid misinterpretations. In this paper, we present an experimental and theoretical analysis of the influence of the sample optical density (OD) at the excitation energy on the results of ultrafast spectroscopy studies in NCs. We show that the pump beam depletion caused by high ODs can drastically change the results from transient absorption (TA) experiments leading to data misinterpretations, such as the overestimation of the optical gain threshold. Based on that, we propose a robust modification on the TA technique, which allows for an OD-independent characterization, free of distortions. The modification consists of pumping the sample below its band gap energy, limiting the electronic excitation to a two-photon absorption process, resulting in an effectively zero OD for the pump beam and a uniform excitation in the direction of the beam propagation. Consequently, an undistorted TA signal is produced, allowing for precise characterization of NCs, including the gain/absorption cross section, gain coefficient, and gain threshold. Furthermore, the uniform excitation allows for higher signal-to-noise ratio, independent of the sample concentration.



KEYWORDS: *quantum dots, pump and probe, transient absorption, optical gain, gain threshold, gain coefficient, two-photon absorption*

The natural vocation of colloidal semiconductor nanocrystals (NCs) for optoelectronic applications made optical characterization essential for advances in the field. Indeed, optical techniques, in particular, ultrafast spectroscopy techniques, have played an important role in answering fundamental questions, which are vital for the development of NC-based technologies.[1] For example, understanding electronic processes, such as multiexciton interactions[2−6] or carrier relaxation dynamics,[7] through ultrafast optical spectroscopy, is crucial to design new materials, aiming the application in lasers,[8−10] LEDs,[11−13] and sunlight-harvesting devices.[14,15] A particularly relevant ultrafast optical spectroscopy technique in the field of colloidal NCs is transient absorption (TA). With this experiment, it is possible to measure the excited state dynamics of colloidal nanostructures, elucidating the fundamental mechanisms, which dictate the excitonic relaxation processes in these materials.[16−18] Due to the limited size of these nanostructures, several processes involved in the exciton dynamics are dependent on the number of excitons created per nanomaterial; consequently, it is crucial that one knows the excitation density at which the optical experiment is being performed.[19]

In this scenario, a relevant parameter for any optical characterization technique is the optical density (OD).[20] The OD characterizes how light is attenuated while traveling within some media. In TA experiments, the OD at the pump wavelength (which is proportional to the NC concentration in a colloidal suspension) directly affects how uniform is the excitation experienced by the probe in the direction of the beam propagation. This means that the higher the OD at the pump wavelength, the less uniform is the excitation experienced by the probe beam. At the same time, simply reducing the NC concentration to reduce the OD is not always

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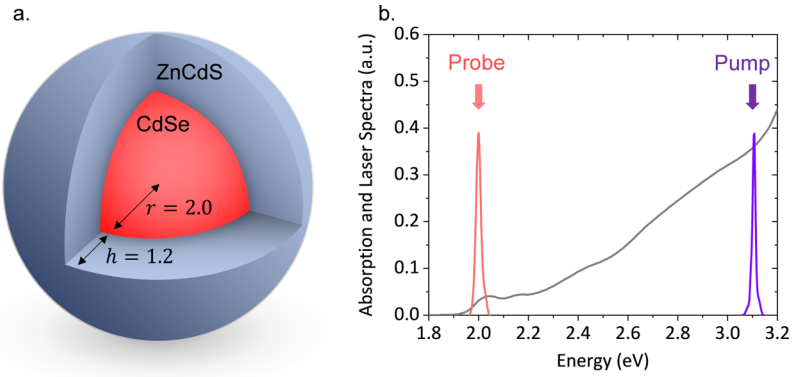

Figure 1. (a) Structure and composition of the studied CdSe/ZnCdS sample. (b) Sample's absorption (gray curve), probe (red curve), and pump (purple curve) spectra.

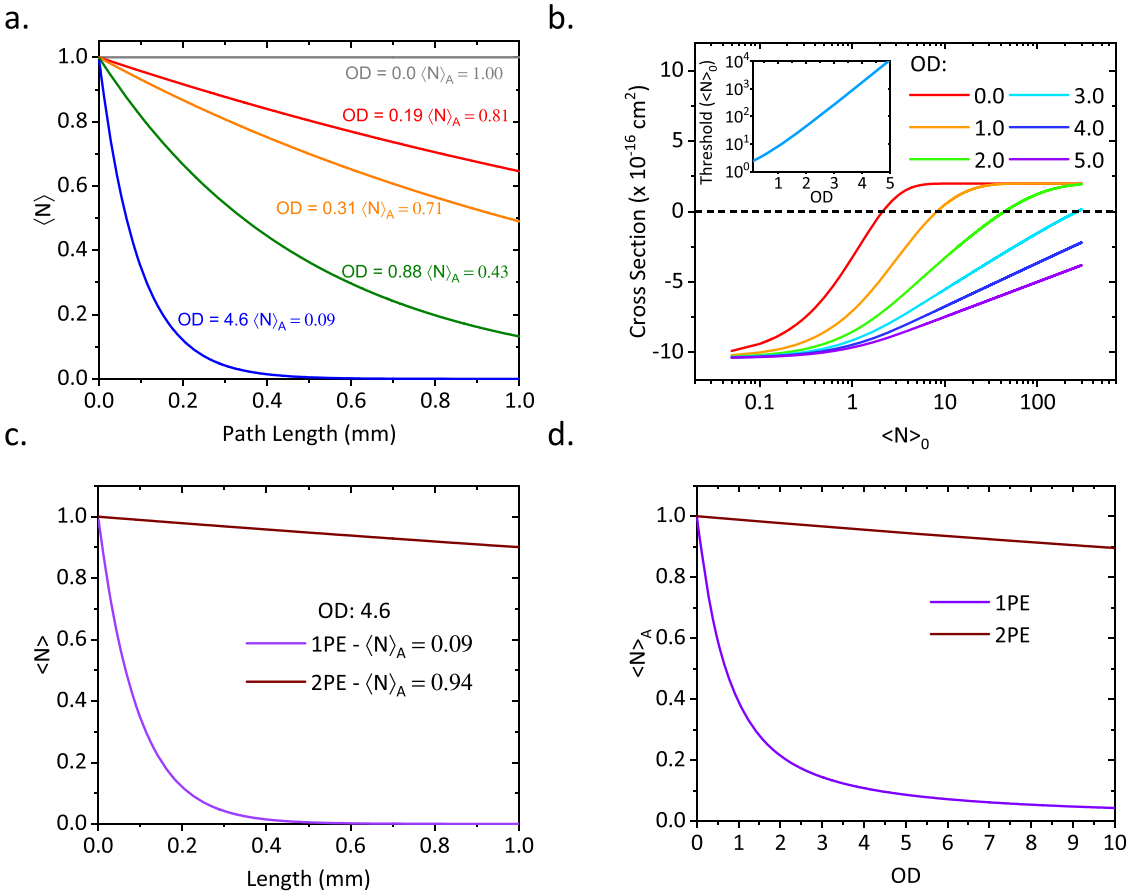

Figure 2. (a) Simulated excitation depletion for the studied sample as a function of the path length, varying the OD. (b) Simulated cross section as a function of $\langle N\rangle_0$ for different ODs. (c) Comparison of the beam depletion for a 1PE and 2PE process under an OD of 4.6 in a path length of 1 mm. For the 2PE simulation, we considered an excitation with pulse width of 90 fs and two-photon absorption cross section at 1.55 eV of 10 739 GM. (d) Spatial-averaged number of excitons per NC, $\langle N\rangle_A$, as a function of the OD for 1PE and 2PE processes. All of the parameters used in the simulations are the same as used in panel (c).

a possible solution as a lower OD can also be problematic because the obtained TA signal is proportional to the number of probed nanoparticles, which is proportional to the OD at the probe wavelength (i.e., the NC concentration).

Circumventing the effect of nonuniform excitation due to OD is a major concern when performing TA experiments. For instance, Li and Lian[21] have shown that aspects of the gain threshold in CdSe nanoplatelets could have been erroneously related to size dependence because the sample OD has not been taken into account. The most common strategy to avoid this issue is to dilute the studied sample to decrease its OD.[4,17,22] Although this suppresses light attenuation, this strategy is not always viable. For instance, while this strategy works for nanoplatelets, in which the OD varies slowly with the wavelength, in some heterostructured core/shell NCs, the absorption coefficient greatly increases at higher energies, due to the shell absorption, which makes it a hard task to unite low ODs at the pump wavelength and high-enough concentration

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ACS Photonics XXXX, XXX, XXX−XXX

to obtain a measurable signal at the probe wavelength.[6] In these cases, an alternative is to perform the experiment with pump energies closer to the band gap. However, this alternative has two main limitations: first, it avoids excitation at the shell levels, reducing what one can learn from the shell influence on the exciton dynamics. Second, if the pump energy is too close to the band gap, the possible number of generated excitons is limited by the degeneracy of the quantized NC states, and state filling needs to be considered for correct characterization. Another used strategy is to consider the beam depletion during the analysis of the obtained data by simply assuming an averaged excitation throughout the cuvette.[23] However, as shown in this paper, this strategy does not completely circumvent the effect of beam depletion, in particular, for experiments to determine optical gain thresholds.

Based on that, in this letter, we discuss the influence of the OD at the pump energy on the optical gain characterization of NCs, showing that the methods typically employed to circumvent this problem do not always work, particularly, for heterostructures, in which the OD drastically increases at higher energies. We offer an alternative way to obtain uniform excitation on TA experiments, allowing for a faster and more reliable determination of fundamental processes in nanomaterials. This is done by simply switching the excitation from the typical one-photon pumping to a two-photon excitation (2PE) process. Since 2PE allows excitation by photons with energies below the band gap, the effective OD at this wavelength is negligible. Therefore, a uniform excitation in the beam propagation direction can be produced, nearly independent of the nanoparticle concentration in the sample. Consequently, a more accurate measurement of relevant parameters is allowed, such as the stimulated emission cross section or optical gain coefficients and threshold. Moreover, due to the near independence to the sample concentration, it is possible to acquire TA signals with signal-to-noise ratio orders of magnitude higher than those acquired by 1PE, allowing for faster and more accurate experiments.

RESULTS AND DISCUSSION

As a proof of concept on how OD affects the obtained results in TA experiments, we study the effect of the OD on the optical gain characterization of a typical core/shell NC, with a CdSe core and a ZnCdS shell of 2.0 and 1.2 nm of mean radius and thickness, respectively. The sample structure and absorption spectrum are shown in Figure 1a,b, and the synthesis procedure is described in detail in refs 24, 25.

A conventional TA experiment uses two beams: the first (pump) excites the sample generating an excited population, and the second, probes some desired transitions after the excitation.[1,26] The detected signal is obtained after the probe beam goes through the sample, which means that the obtained signal will result from a contribution of all excited populations in the beam path. However, since the excitation beam is attenuated due to absorption, the generated population will not be uniform through the propagation direction.

Following the Beer–Lambert law, disregarding the effect of scattering, the average number of excitons generated though the beam path decays as $\langle N\rangle(z) = \langle N\rangle_0 \cdot e^{-OD \cdot \ln 10 z/L}$, in which $\langle N\rangle_0$ and L are the average number of excitons in the sample's front surface and the length of the beam path, respectively. Note that, for the sake of simplicity, we consider here a pump that is uniformly distributed in the radial direction, i.e., the pump waist is much larger than the probe one. So, considering an experimental situation in which the sample is kept inside a 1 mm analytical cell, with an initial excitation of $\langle N\rangle_0 = 1$, Figure 2a describes how the excitation decays through the sample according to the OD. Because the excitation is not uniform, it is useful to define a spatial-averaged number of excitons, $N_A = \frac{1}{L}\int_0^L N(z)\,dz$, generated through the beam path. By doing so, in Figure 2a, we can see that even for a small OD of 0.19, $\langle N\rangle_A$ is nearly 20% lower than $\langle N\rangle_0$.

By predicting how the excitation changes through the beam path, we can simulate how this effect can cause distortions in the results of TA experiments. To illustrate that, we study an important parameter that modulates light–matter interactions, the sample's optical absorption, and stimulated emission cross section (σ). Although σ is an intrinsic property of an individual NC, we can measure the ensemble-averaged cross section, σ_A, using TA. This is a useful quantity since it gives important information about how light interacts with individual nanoparticles in the sample, on average. For example, if $\sigma_A > 0$, on average, the nanoparticles have a higher probability of interacting with light via stimulated emission than by absorption. Details of how to calculate σ_A can be found in Section S1 of the Supporting Information (SI).

To study the impact on the ensemble-averaged cross section with the OD, we simulated the probe centered at 2.0 eV and the pump at 3.1 eV, as illustrated in Figure 1b. The probe energy was set to have an energy slightly below the band gap, which is the optimum region to generate optical gain in type-I core/shell nanostructures. After the carriers are excited by the pump, they quickly relax to the band edge. By increasing the excitation intensity, the number of generated excitons also increases, changing the interaction characteristics of the probe with the sample. As $\langle N\rangle_0$ increases, the sample goes from an absorptive regime ($\sigma_A < 0$) to an optical gain regime ($\sigma_A > 0$), as is shown in Figure 2b. However, as expected, the value of σ_A is greatly impacted by the OD. For a given $\langle N\rangle_0$, σ_A decreases as the OD increases. This means that the measurement of some important parameters is also greatly impacted by the OD. For example, if we consider the optical gain threshold, $\langle N\rangle_{Tr}$, it increases from ~1 for ODs close to zero, to unrealistic values for ODs close to 4, as is shown in the inset of Figure 2b. The same happens to other relevant parameters for the NC characterization, such as the absorption/gain coefficient, as shown in Section S2 of the SI.

A way to mitigate the effect of this distortion is to consider the spatial-averaged number of excitons per NC, $\langle N\rangle_A$, instead of $\langle N\rangle_0$.[23] For low concentrations, this approximation greatly reduces the distortions. However, due to the nonlinear dependence of the measured parameters with $\langle N\rangle$ (or with the fluence), the dependence of σ_A with the OD cannot be totally suppressed by this method. As is shown in detail in Section S3 of the SI, this method is valid only for relatively small ODs (<1.0) as it overestimates the optical gain threshold by about 50% when the OD at the pump energy is 1.0.

Now, considering a 2PE process, in which we use photons with energy below the material's band gap to excite the sample, the effective OD reaches negligible values. In Figure 2c, we show a simulation of the difference in the beam depletion for a one-photon excitation (1PE) and 2PE processes for a highly concentrated sample (OD of 4.6 at the excitation wavelength and path length of 1 mm). In this analysis, we simulate an experimental condition using the 1PE and 2PE with photon

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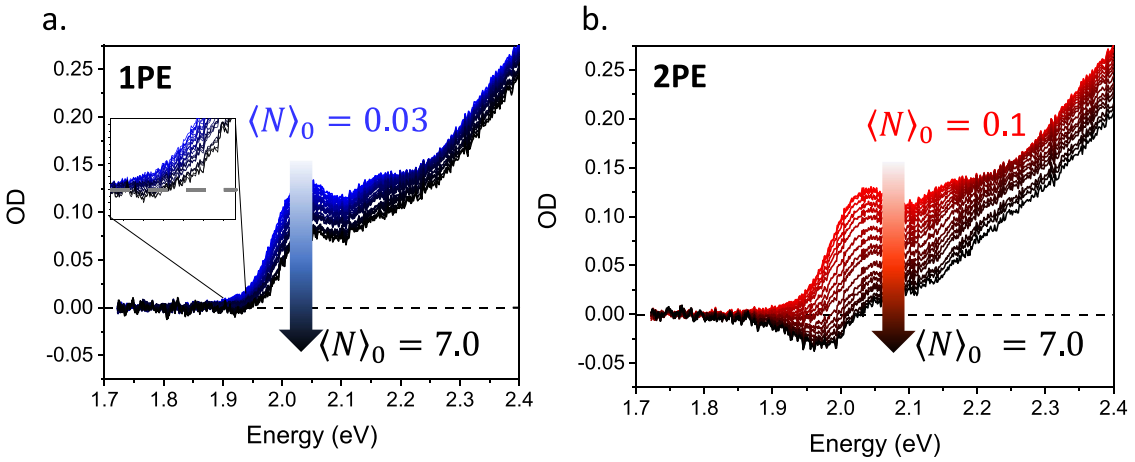

Figure 3. TA data obtained with a broadband probe spectrum under (a) 1PE and (b) 2PE. In panel (a), the inset shows a zoom of the optical gain band for 1PE. For 1PE, the photon energy of the pump is set to 3.1 eV, meanwhile, for 2PE, it is 1.55 eV. More experimental details of the broadband TA can be found is Section S5 of the SI. For this experiment, the OD at 3.1 eV is 1.14.

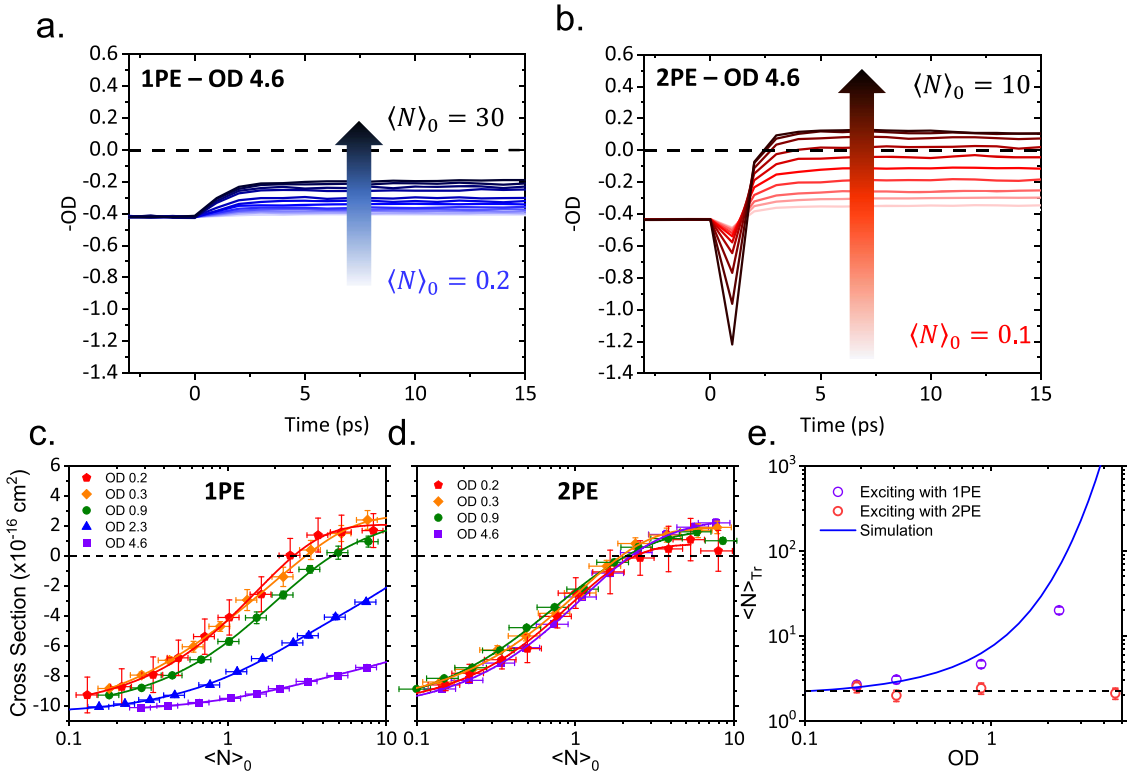

Figure 4. TA data under (a) 1PE and (b) 2PE for the sample with an OD of 4.6 at 3.1 eV. For these experiments the pump and probe energies were set to 3.10 and 2.00 eV, respectively. The initial dip shown by the data under 2PE in panel (b) is an artifact due to the solvent. The analysis of this feature is presented in detail in Section S7 of the Supporting Information (SI). Effect of the OD on the ensemble-averaged cross section, σ_A, as a function of $\langle N\rangle_0$, under (c) 1PE and (d) 2PE. (e) Comparison of the optical gain threshold obtained experimentally under 1PE (purple circles) and 2PE (red circles) with the simulation (blue curve). The dashed black line is a horizontal line to guide the eyes.

energies of 3.10 and 1.55 eV, respectively, which excites the sample to transitions well above the band gap energy and above the shell band gap. This means that even though the 1PE and 2PE processes have different selection rules,[27,28] we are accessing transitions with similar energy, as in this range, the density of states reaches a quasicontinuum. From the simulations, we can see that in the 1PE process, the excitation rapidly decays through the beam path, generating a spatial-averaged excitation of $\langle N\rangle_A = 0.09$. Meanwhile, for the 2PE process, the excitation is nearly uniform, generating $\langle N\rangle_A = 0.94$. In fact, as we can see in Figure 2d, even for ODs close to 10, the excitation continues nearly uniform through the beam path. It is important to note that in the 2PE process, the absorption is proportional to the square of the excitation intensity. This means that as the excitation intensity increases, the effective OD in the 2PE process also increases. We describe in detail how this affects beam depletion in a 2PE process in Section S4 of the SI.

To validate the proposed simulations, we compared the results of a TA experiment under 1PE and 2PE. Similar to the

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ACS Photonics XXXX, XXX, XXX−XXX

simulations, the pump was set to excite the sample at 3.10 eV (corresponding to photon energy at 3.10 eV for 1PE and 1.55 eV for 2PE). More details about this experiment and sample preparation can be found in Section S5 of the SI. For this experiment, the OD of the sample at 3.10 eV was set at 1.14 to highlight the differences between 1PE and 2PE, as shown in Figure 3a,b. For 1PE, as shown in Figure 3a, the photobleach increases as the pump intensity increases, however, an optical gain feature (OD < 0) appears weakly, even at high excitation regimes ($\langle N\rangle_0 \sim 7.0$). On the other hand, under 2PE (Figure 3b), a clear optical gain band (OD < 0) emerges for $\langle N\rangle_0 \sim 1.5$ slightly below the band gap energy.

To quantify the influence of the OD on the signal observed in Figure 3, we investigated the optical gain slightly below the sample's band gap (2.00 eV) for different ODs under 1PE and 2PE (details in Section S5 of the SI). To generate optical gain, the pump energy was set to 3.1 eV (1PE) and 1.55 eV (2PE). Figure 4a,b shows TA data for an OD of 4.6 at 3.1 eV. Likewise, in Figure 3a,b, for high OD, optical gain can be easily detected under 2PE but not under 1PE. From this data, we calculate the experimental values for the absorption and stimulated emission cross sections (calculated according to eq S6 of the SI) and compare them with the simulation presented in Figure 2b. Repeating the same experiment for other sample concentrations (i.e., different OD's) we observe that, as predicted by the simulations shown in Figure 2b, due to the pump beam depletion, the measured optical gain threshold increases for higher ODs, being undetectable for the highest concentration (Figure 4c). On the other hand, as shown in Figure 4d, the profile of the gain curves barely changes for 2PE, even when the concentration is increased by over one order of magnitude. The threshold measured under 2PE is similar to the one obtained under 1PE at the lowest concentration. Indeed, by comparing the measured optical gain thresholds under 1PE and 2PE with our simulation for 1PE, as shown in Figure 4e, it is evident that TA under 1PE can overestimate the optical gain threshold, whereas 2PE generates the real value, free of distortion. This demonstrates that using 2PE to create population inversion circumvents the distortions on a TA measurement due to the OD. The same rationale is true for the study of any excitonic dynamics, which relies on the precise determination of the number of excitons created per nanoparticle.

It is important to emphasize that obtaining the correct relationship between the pump intensity and $\langle N\rangle_0$ is fundamental, regardless the pump is 1PE or 2PE. To minimize the experimental errors when determining this relationship for TA measurements under 2PE, we determined the two-photon absorption cross section by a multiphoton absorption photoluminescence saturation (MPAPS) technique,[29] using the exact same pump alignment, by simply blocking the probe beam and collecting the emitted photoluminescence as a function of the pump fluence. Then, the values for $\langle N\rangle$ are obtained following the method discussed in ref 29 with an overall estimated error of ~15%.[29] For 1PE, $\langle N\rangle_0$ was obtained through the sample's linear absorption cross section, which was measured following the procedure detailed in Section S6 of the SI.

Pumping the sample with 2PE offers other advantages in relation to 1PE. Perhaps, the most striking difference is the higher magnitude of the TA signals, due to the more uniform excitation, which creates nearly the same excitation density from the front to the back surface of the sample. As the TA signal is proportional to the number of excited nanoparticles, the combination of 2PE and high OD results in larger signals, drastically improving the signal-to-noise ratio. For instance, to have an OD lower than 0.3 at the excitation wavelength using 1PE, we would need to have an OD of 0.033 at the band edge. In principle, the same result could be obtained under 2PE, even using samples with concentration orders of magnitude higher, obtaining higher signals.

Therefore, in situations on which the absorption varies only weakly with the excitation energy, which is the case for core-only quantum dots and nanoplatelets,[21] it is feasible that one keeps the nanoparticle concentration low enough to allow correct characterization by 1PE, with minimum distortions caused by beam depletion. On the other hand, the results presented here are particularly important for samples on which the absorption increases significantly with the excitation energy, which is the case for core/shell heterostructures such as giant dots,[30] spherical quantum wells,[6] or dot-in-rod[31] samples. In thick shell heterostructures, for instance, the absorption at the near-UV range increases drastically compared to one at the band edge, being up to 2 orders of magnitude larger. In situations like this, keeping the OD below 0.3 above the shell band gap would result in an OD at the band edge below 0.003, making the near band edge TA signal virtually indetectable. Consequently, obtaining reliable TA data for samples like this is very challenging using the conventional 1PE TA experiment. We exemplify this fact in Section S8 of the SI, where we describe the change in absorption for spherical quantum well samples with a thick outer shell.

Although all of the results that we presented here are limited to the analysis of the optical gain in colloidal nanostructures based on the TA experiment, the same rationale can be expanded to the analysis of other physical processes interrogated by TA techniques, including exciton and multiexciton dynamics, intraband relaxation, change transfer, etc. Furthermore, it is not limited to colloidal nanomaterials, being applicable to other optical materials, such as bulk semiconductors and organic nanostructures.

CONCLUSIONS

To conclude, we have demonstrated that the sample OD at the pump energy is a key factor that needs to be considered when characterizing optical materials with TA experiments, in particular, for those experiments in which the measured parameter depends on the excitation density. The distortions in the signal caused by high ODs may lead to data misinterpretation. We offered a simple, yet effective solution to the problem: exchange the typical above band gap excitation by a below band gap excitation via two-photon absorption. To prove this concept, we investigated optical gain properties on a sample of colloidal CdSe/CdZnS core/shell quantum dots as a function of its concentration, by varying its OD by nearly 2 orders of magnitude. We demonstrated that, while under one-photon excitation, the optical gain properties strongly depend on the OD; for two-photon excitation, the results are independent of the sample OD, and we could obtain the real value for the gain threshold and stimulated emission cross section independently of the sample concentration.

Besides avoiding distortions, in the case of colloidal samples, this modification allows TA experiments to be performed in high concentrated suspensions, which can also increase the detected signal by orders of magnitude, transforming a time-consuming TA into a faster and more reliable experiment.

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ACS Photonics XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

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Details on the calculation of σ_A; influence of the OD on the measurement of the gain coefficient, using the spatial average of excitons instead of the excitation on the front surface of the sample; influence of the OD and $\langle N \rangle_0$ on the depth penetrability in a two-photon absorption process; details on the transient absorption experiment; measurement of the one-photon absorption cross section; influence of the solvent; and problem of conventional 1PE TA for characterizing thick shell heterostructures (PDF)

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Notes

The authors declare no competing financial interest.

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