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2007 J. Phys.: Condens. Matter 19 486208

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Fluorescence correlation spectroscopic study on water-soluble cadmium telluride nanocrystals: fast blinking dynamics in the μs –ms region

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Received 10 June 2007, in final form 17 October 2007

Published 9 November 2007

Online at stacks.iop.org/JPhysCM/19/486208

Abstract

We have examined the relaxation dynamics of the dark state for water-soluble cadmium telluride (CdTe) nanocrystals by fluorescence correlation spectroscopy (FCS). Autocorrelation curves for CdTe nanocrystals were not reproduced by an analytical model including a single diffusion term and monophasic decay of dark-state contribution, but well reproduced by a model taking into account stretched-exponential type nonradiative relaxation. The present result suggests the presence of a widely distributed relaxation pathway of the dark state in the time region from μs to ms. Data analysis by the model including stretched-exponential type decay revealed that the timescale of nonradiative relaxation for CdTe nanocrystals decreased with the excitation laser power, suggesting the relaxation process of the dark state is promoted by additional absorption of a photon.

1. Introduction

Since the development of a stabilizing method for semiconductor nanocrystals in solution [1, 2], the emissive colloidal nanocrystals, so-called quantum dots, have been attracting considerable attention owing to their extreme brightness and higher photostability than that of organic fluorescent molecules. In quantum dots ranging from 1.5 to 8 nm in diameter, the confinement

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energy of an exciton (a pair of an electron and a hole) is higher than that of electrostatic interaction, resulting in the quantized energy level for an exciton depending on the size of a quantum dot. Hence, the emission color of a quantum dot can be tuned from the visible to the near-infrared region by control of the particles' size.

In order to optimize these excellent advantages of quantum dots, it is indispensable to get an insight into the relaxation dynamics of the excited states for semiconductor nanocrystals that is quite different from those of organic fluorescent molecules. Since the first observation of intermittency for a single quantum dot [3], many investigations have revealed substantial heterogeneity in their relaxation dynamics from the excited state both via emissive and via nonradiative pathways. Techniques for single-molecule detection (SMD), such as confocal microscopy and wide-field imaging by a highly sensitive CCD camera, have been applied to investigation of the blinking behavior of quantum dots by a number of groups. One of the most significant results obtained by single-particle measurements is that the on/off time distribution of a quantum dot follows power-law statistics [4, 5] in the time region from several tens of milliseconds to hundreds of seconds. The most important consequence of the power law statistics is that the average on/off time of quantum dots is dependent on the measurement (integration) time, i.e. the timescale of the blinking depends on observation time.

However, previous approaches using single-particle detection methods, such as the combination use of a confocal microscope with avalanche photodiodes and/or wide-field imaging by a back-illumination CCD camera, needed the immobilized condition for the quantum dot under observation, and rather long integration time (typically >10 ms) for the reliable detection of the on/off time. The immobilization in an amorphous solid usually serves as an inhomogeneous environment for each quantum dot; in addition the long integration time prevents detection of the dynamic behaviors in a shorter time region. Both limitations make it difficult to elucidate the origin of the dispersive kinetics of the quantum dot.

To provide homogeneous conditions and to get better temporal resolution in the detection of quantum dots at single-particle level, fluorescence correlation spectroscopy [6, 7] (FCS) can be potentially applied for characterization of their photophysical properties. However, in spite of the potential for getting an insight into the blinking at a faster temporal scale than that in the approach using SMD, only a handful of studies on quantum dots by FCS have been published up to now [8–11]. Especially, studies on CdTe nanocrystals by FCS have not yet been published as far as we know. In the present paper, we have applied the FCS to the measurement of the blinking for CdTe quantum dots in water so that we may characterize the timescale of the 'off' time on the basis of the autocorrelation function obtained.

2. Materials and methods

CdTe nanocrystals with different sizes were synthesized according to the procedure in the report of Weller *et al* [12]. The sizes of the CdTe nanocrystals were estimated from their steady-state absorption/emission spectrum using a calculation result on the relation between band-gap and particle size for CdTe nanocrystals in the literature [13]. The observation of the CdTe nanocrystals by a transmission electron microscope also provided comparable values of particle size (data not shown) to this estimation. The dilute colloidal suspension (typically $\sim 10^{-9}$ M order) of the CdTe nanocrystals in water was injected into glass-bottom culture dishes (MatTek) for measurement.

The experimental set-up for the FCS measurement consisting of a home-built confocal microscope and a CW laser is schematically illustrated in figure 1. As an excitation light source for the FCS measurement, a CW Ar⁺ laser (LGK7872M, LASOS lasertechnik) oscillating at 488 nm was coupled to a single-mode optical fiber to isolate the light source from the

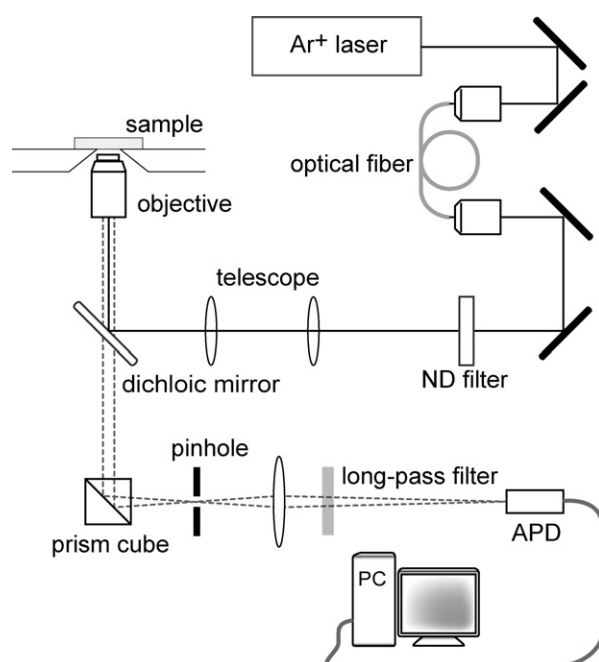


Figure 1. Schematic illustration of the FCS system used in the present work. The excitation laser light from a cw-Ar⁺ laser (488 nm) passing through an optical fiber was re-collimated by a pair of lenses, then was focused by a high-NA objective (NA 1.35, 100 \times) close to its diffraction limit. The focusing point of the laser beam was controlled by the pairs of lenses both in the focal plane and along the optical axis of the objective.

optical bench on which the set-up is constructed. After passing through the optical fiber, the excitation laser beam was re-collimated with a pair of lenses, and then was tightly focused by a microscope objective (UPlanApo 100 \times Oil Iris3, NA 1.35, Olympus). In the present series of experiments, pinholes with 25, 50, or 100 μm diameters were attached to an optical microscope (IX70, Olympus) for realizing confocal optical configurations with different sampling volumes. The emitted photons from the quantum dots inside the confocal (sampling) volume were detected with an avalanche photodiode (SPCM-AQR-14, Perkin Elmer) connected with a counting board (M9003, Hamamatsu Photonics K.K.). Stray light of 488 nm propagating to the avalanche photodiode was blocked by a long-pass filter (Semrock, LP01-488RU). The autocorrelation function (ACF) of the photoluminescence intensity was calculated using FCS software (U9451, Hamamatsu Photonics K.K.) from the integrated data of photons for ~ 3 s. Through all measurements in the present study, the focusing point of the blue laser was located 30 μm above the bottom of the culture dishes. All experiments described in the present articles were conducted at room temperature (22 ± 0.5 $^{\circ}\text{C}$).

3. Analytical expression of fluorescence correlation signal

Fluorescence correlation spectroscopy provides information on the translational diffusion velocity and the triplet lifetime of fluorescent molecules (dark-state lifetime in the present case) that cause the fluctuation of fluorescence intensity in the time domain. The autocorrelation function, $G(\tau)$, of this fluorescence fluctuation at the confocal volume is analytically derived

by the following equation [7, 14].

$$G(\tau) = 1 + \frac{1}{N} \left(1 + \frac{p}{1-p} \exp\left(-\frac{\tau}{\tau_T}\right) \right) \left(1 + \frac{\tau}{\tau_D} \right)^{-1} \left(1 + \frac{\tau}{w^2 \tau_D} \right)^{-1/2}, \quad (1)$$

where N is the average number of molecules in the confocal volume, V_{conf} , with cylindrical shape, p and τ_T are the fraction of the contribution of triplet state (dark state in organic molecular systems) and its lifetime, respectively, and w is the structure parameter defined by $w = w_z/w_{xy}$. Here, w_z and w_{xy} are respectively the axial length and radial radius of the cylindrical confocal volume ($V_{\text{conf}} = 2\pi w_z w_{xy}^2$). τ_D is the diffusion time related to the translational diffusion coefficient, D , by

$$\tau_D = \frac{w_{xy}^2}{4D}. \quad (2)$$

The analysis of the autocorrelation function obtained on the basis of equation (1) provides the diffusion time, τ_D , and the triplet (dark-state) lifetime, τ_T , of a fluorescent molecule.

As stated in section 1, quantum dots exhibit quite complex nonradiative relaxation dynamics. The nonradiative decay obtained through experiments is not reproduced by a single-exponential curve in contrast to the experimental results of fluorescent organic molecules that are well reproduced by the analytical model expressed by equation (1). In order to parametrize fluorescence correlation signals of quantum dots and to analyze the experimental data quantitatively, here we adopt a fluorescence autocorrelation function including the decay component of stretched exponential relaxation, of which the analytical expression is represented by

$$G(\tau) = 1 + \frac{1}{N} \left(1 + \frac{p}{1-p} \exp\left(-\left(\frac{\tau}{\tau_{\text{dark}}}\right)^\alpha\right) \right) \left(1 + \frac{\tau}{\tau_D} \right)^{-1} \left(1 + \frac{\tau}{w^2 \tau_D} \right)^{-1/2}. \quad (3)$$

Here, τ_{dark} is the characteristic time of the nonradiative relaxation, and α is a stretched factor.

4. Results and discussion

4.1. Absorption and emission spectrum

The steady-state absorption spectrum of the CdTe nanoparticles exhibits distinct peaks of different bands corresponding to each size as shown in figure 2(a), indicating that all of these suspensions include mono-dispersed nanocrystals. This is also supported by their fluorescence spectrum with different peak bands as in figure 2(b).

4.2. FCS measurements

Prior to the discussion on the quantum dot, we show fluorescence autocorrelation curves of rhodamine 6G in ethylene glycol (a) and rhodamine 123 in water (b) in figure 3 as references. Solid lines in these traces are curves calculated by the nonlinear least-square method with equation (1) and residuals are plotted at the top of each trace. The good agreement between these experimental results and the analytical model, equation (1), assures us that the measurement can provide reliable values on the parameters, and that the anomalous autocorrelation curves of CdTe nanocrystals obtained in the present study do not originate in artifacts of the experimental set-up.

As already described in section 2, the lateral size of the volume element, w_{xy} , is related to diffusion time, τ_D , and diffusion coefficient, D . The lateral size of the confocal volume, w_{xy} , for the 25 μm pinhole was determined to be 350 nm in diameter on the basis of

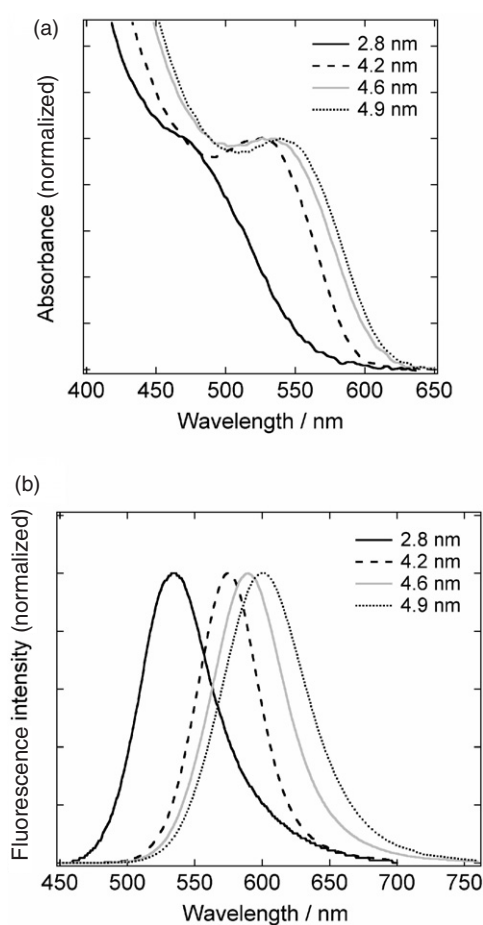


Figure 2. Absorption (a) and emission (b) spectra for water-soluble CdTe nanocrystals examined in the present study.

the diffusion constants of rhodamine 6G ($2.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) [15, 16] and rhodamine 123 ($3.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) [17] in water from the literature as references. The diffusion times for rhodamine 6G and rhodamine 123 were linearly related to the diameters of pinholes used in the present study (25, 50, and 100 μm) as predicted by the theoretical model of equation (1). This confirms again that the series of measurements in the present paper was conducted under ideal conditions.

Figure 4 shows the autocorrelation curve for the CdTe nanocrystal with the diameter of 4.6 nm in water at the excitation power of 100 μW . Curves analyzed by the nonlinear least-square method with equation (1) and with equation (3) are drawn as solid lines with the experimental data (gray dots) with residuals at the top of each trace. The result clearly shows that the experimental data cannot be reproduced by the curve calculated on the basis of equation (1). On the other hand, the result was well reproduced by the curve calculated on the basis of equation (3) that takes into account the stretched-exponential type decay component. This indicates that the dark state has multiple relaxation pathways even in the solution phase. For other suspensions of the nanocrystals, it was also confirmed that the analysis based on equation (3) reproduced experimental results. Clearly distinguishable spectral shift among

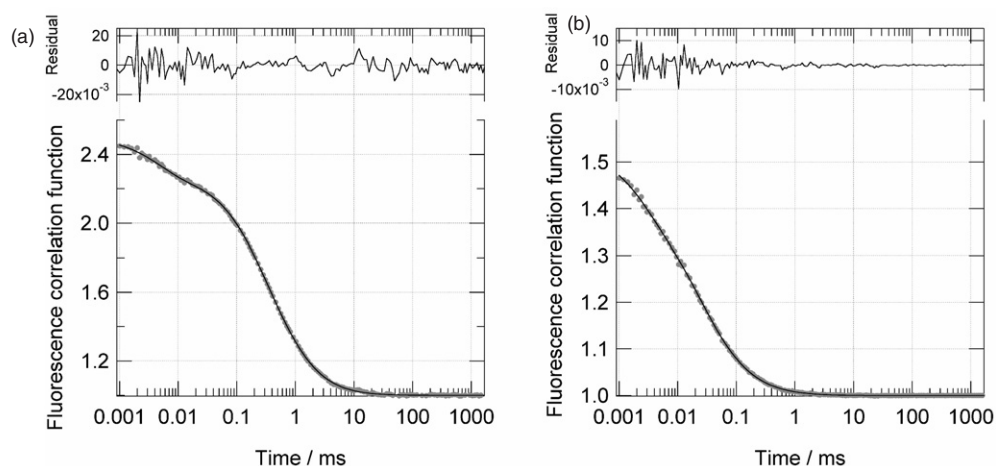


Figure 3. Typical fluorescence autocorrelation curves for rhodamine 6G in ethylene glycol (a) and rhodamine 123 in water (b), showing good agreement between these experimental results and calculation based on the analytical model of equation (1).

CdTe nanocrystals of 4.2, 4.6, and 4.9 nm as in figure 2 can support the monodispersity of these samples; hence, the intrinsic polydispersity of the samples does not account for these anomalous autocorrelation curves, indicating that the anomalous autocorrelation curves of the quantum dots are attributed to multiple relaxation pathways inherent in the nanocrystals.

4.3. Excitation intensity effect

The shapes of autocorrelation curves for the CdTe nanocrystals remarkably depend upon the excitation laser power as is representatively shown in figure 5 for CdTe nanocrystals with size of 4.9 nm in diameter. From the result, it is clearly recognized that the value of the autocorrelation curve at the temporal origin, $G(0)$, decreases with an increase in the excitation laser power (figure 5(a)). The decrease of $G(0)$ value with increasing excitation intensity was also observed for other CdTe quantum dots with different sizes.

The shape of the autocorrelation curve is also dependent on the excitation laser power, as shown in figure 5(b); the decay of autocorrelation becomes faster with an increase in the excitation laser power. Since the solvent (water) does not absorb the excitation laser light, the temperature in the sampling area of the FCS measurement stayed constant [18]; the thermal motion of the quantum dots was not affected by irradiation of the excitation laser beam. Hence, the change in the autocorrelation curve for the CdTe dots in the temporal region from μs to ms can be attributed to the blinking. We plot values of τ_{dark} as a function of diffusion time for each sample in figure 6. The value of τ_{dark} shows overall linear dependence on the diffusion time at the same excitation laser power. In this data analysis, the parameter, τ_{dark} , was obtained by the nonlinear least-square method with constant τ_{D} values determined from diameters of the nanocrystals and the viscosity of water under the assumption that the diffusion time of a nanocrystal is not seriously affected by the intensity change of the excitation laser light.

The parameter, τ_{dark} , which is a representative of timescale for nonradiative relaxation dynamics in a quantum dot, is also dependent on the excitation laser power; the value of τ_{dark} determined by the analysis with equation (3) decreases with increasing excitation laser power. All values of τ_{dark} are plotted as a function of the excitation laser power from 10 to

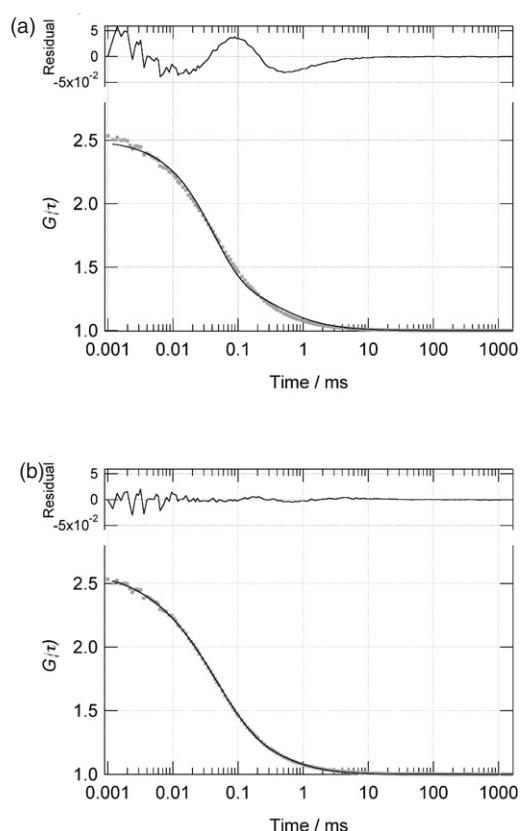


Figure 4. Typical fluorescence autocorrelation curve (gray dots) of the CdTe nanocrystals with 4.6 nm diameter in water with a calculated curve (solid line) based on equation (1) (a) and based on equation (3) (b). Gray dots in these graphs show the same experimental result on the CdTe nanocrystals. Residuals are also drawn at the top of each trace.

200 μW in figure 7. All particles with different sizes exhibit a similar trend, that is, values of τ_{dark} monotonically decrease with increasing excitation laser power for all kinds of particles examined. As was described above, the value of τ_{dark} increased in proportion to the diffusion time (observation time); smaller particles with shorter τ_{D} exhibited shorter τ_{dark} . This explains the dependence of τ_{dark} on particle size at the same excitation power in figure 7.

A decrease of $G(0)$ with increasing excitation power was previously observed by Larsen *et al* in the two-photon FCS measurement for CdSe quantum dots [8]. They attributed the excitation intensity dependence to excitation saturation. As is shown in the inset of figure 5(a), the fluorescence intensity detected in the present study exhibited excitation saturation somewhat. The saturation effect, however, predicts an apparently slow diffusion time [19]. Contrary to this prediction, the decay of the autocorrelation shown in figure 5(b) exhibited the opposite dependence on the excitation intensity; similar trends were also reported by Weiss *et al* [9] and by Cramb *et al* [20]. These results, including ours, indicate that the simple saturation effect cannot account for the changes in the shape of the autocorrelation curves.

By integrating the above discussion with the dependence of τ_{dark} on the excitation intensity, it is strongly suggested that the detrapping process of a carrier from trap sites is accelerated by the absorption of the exposed light. The depth of trap sites may have a distribution and affect

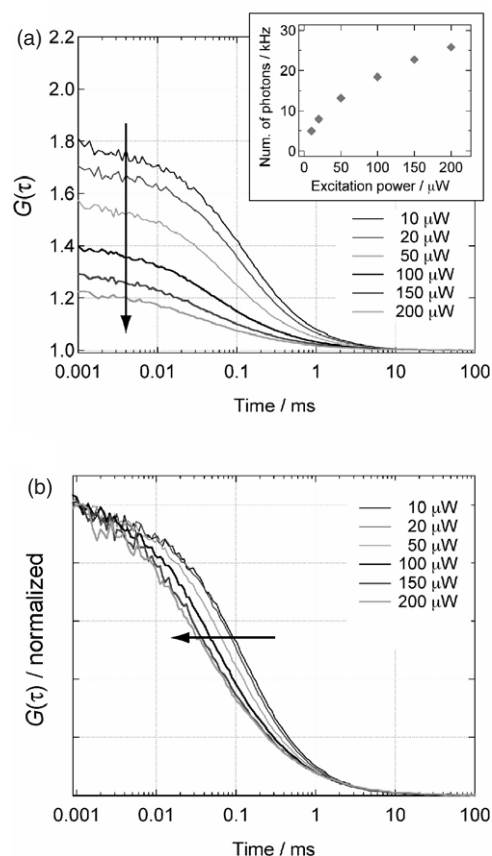


Figure 5. Change in overall shape of the autocorrelation curve for CdTe nanocrystals with size of 4.9 nm in diameter depending on the excitation laser power (a) and comparison of the shape of these autocorrelation curves by normalization (b). The inset of figure 5(a) shows the number of photons counted versus the excitation laser power.

the dispersive kinetics. On this point, we are now working on the model calculation, of which the result will be published soon.

5. Conclusion

We have examined the relaxation dynamics of the dark state for CdTe nanocrystals in water using fluorescence correlation spectroscopy. In comparison to the approach by single-particle detection methods for quantum dots immobilized in/on solids, the present approach can provide information on the dark state of mobile quantum dots in solution with higher temporal resolution. The autocorrelation curves for the CdTe nanocrystals were not reproduced by the analytical model of FCS including a single diffusion term and a monophasic dark-state contribution, but well reproduced by the analytical model taking into account stretched-exponential type relaxation. This strongly suggests the widely distributed relaxation pathway of the dark state in the timescale from μs to ms.

The value of τ_{dark} determined through the present study exhibited excitation power dependence, suggesting the relaxation process of the dark state promoted by additional

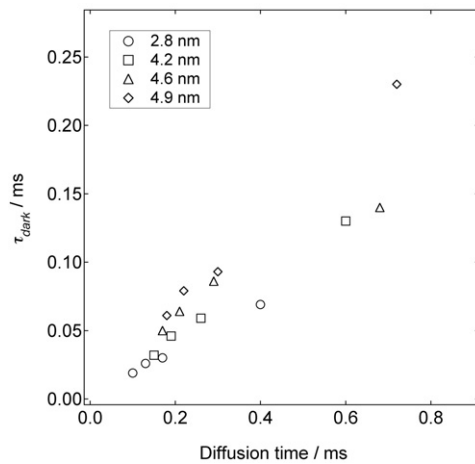


Figure 6. Values of τ_{dark} as a function of corresponding diffusion times (observation times) for each CdTe nanocrystal. Four kinds of experiments for one sample were conducted under different experimental conditions on the size of a pinhole and solvent as follows: (1) 25 μm pinhole, in water; (2) 25 μm pinhole, in deuterated water; (3) 50 μm pinhole, in water; (4) 100 μm pinhole, in water. All fluorescence correlation signals were measured at the same excitation laser power ~ 50 mW through this series of experiments.

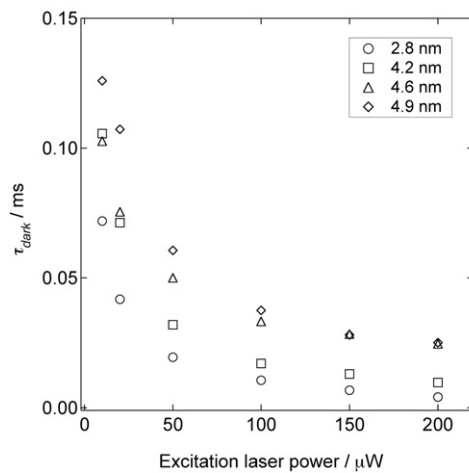


Figure 7. Value of τ_{dark} as a function of the excitation laser power for each CdTe nanocrystal in water.

absorption of a photon in the time region less than 10 ms. This result cannot be obtained by the single-particle detection method using a confocal microscope for immobilized quantum dots.

Acknowledgments

The present work was financially supported by the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), a Grant-in-Aid for Scientific Research on Priority Area ‘Molecular nano dynamics’ and a Grant-in-Aid for Young Scientists (B), the 21st Century

COE Program 'Core Research and Advanced Education Center for Materials Science and Nano Engineering' from the Japan Society for the Promotion of Science (JSPS) and the CREST program of the Japan Science and Technology Agency (JST).

References

- [1] Peng X, Schlamp M C, Kadavanich A V and Alivisatos A P 1997 *J. Am. Chem. Soc.* **119** 7019
- [2] Dabbousi B O, Rodriguez-Viejo J, Mikulec F V, Heine J R, Mattoussi H, Ober R, Jensen K F and Bawendi M G 1997 *J. Phys. Chem. B* **101** 9463
- [3] Nirmal M, Dabbousi B O, Bawendi M G, Macklin J J, Trautman K, Harris T D and Brus L E 1996 *Nature* **383** 802
- [4] Kuno M, Fromm D P, Hamann H F, Gallagher A and Nesbitt D J 2000 *J. Chem. Phys.* **112** 3117
- [5] Shimizu K T, Neuhauser R G, Leatherdale C A, Empedocles S A, Woo W K and Bawendi M G 2001 *Phys. Rev. B* **63** 205316
- [6] Magde D, Elson E L and Webb W W 1974 *Biopolymers* **13** 29
- [7] Rigler R and Elson E S (ed) 2001 *Fluorescence Correlation Spectroscopy (Springer Series in Chemical Physics vol 65)* (Berlin: Springer)
- [8] Larson D R, Zipfel W R, Williams R M, Clark S W, Bruchez M P, Wise F W and Webb W W 2003 *Science* **300** 1434
- [9] Doose S, Tsay J M, Pinaud F and Weiss S 2005 *Anal. Chem.* **77** 2235
- [10] Yao J, Larson D R, Vishwasrao H D, Zipfel W R and Webb W W 2005 *Proc. Natl Acad. Sci.* **102** 14284
- [11] Swift J L, Heuff R F and Cramb D T 2006 *Biophys. J.* **90** 1396
- [12] Gaponik N, Talapin D V, Rogach A L, Hoppe K, Shevchenko E V, Kornowski A, Eychmuller A and Weller H 2002 *J. Phys. Chem. B* **106** 7177
- [13] Pérez-Conde J, Bhattacharjee A K, Chamarro M, Lavallard P, Petrikov V D and Lipovskii A A 2001 *Phys. Rev. B* **64** 113303
- [14] Krichevsky O and Bonnet G 2002 *Rep. Prog. Phys.* **65** 251
- [15] Magde D, Elson E L and Webb W W 1974 *Biopolymers* **13** 29
- [16] Dorn I T, Neumaier K R and Tampe R J 1998 *J. Am. Chem. Soc.* **120** 2753
- [17] Masuda A, Ushdia K and Okamoto T 2005 *Biophys. J.* **88** 3584
- [18] Ito S, Sugiyama T, Toitani N, Katayama G and Miyasaka H 2007 *J. Phys. Chem. B* **111** 2365
- [19] Gregor I, Patra D and Enderlein J 2005 *Chem. Phys. Chem.* **6** 164
- [20] Heuff R F, Swift J L and Cramb D T 2007 *Phys. Chem. Chem. Phys.* **9** 1870