

Three-photon excited band edge and trap emission of CdS semiconductor nanocrystals

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We report on three-photon excited band edge and trap emission of CdS semiconductor nanocrystals. While the band edge emission intensity clearly shows a cubic dependence on excitation intensity, demonstrating three-photon absorption process, the trap emission does not exhibit such a cubic dependence. A simple theoretical model based on the assumption that there exist a limited number of trap states in nanocrystals shows good agreement with the experiment, suggesting that the number of trap states play an important role in their emission intensity dependence of multiphoton excitation. The three-photon absorption cross section of CdS nanocrystals is measured to be $\sim 10^{-79} \text{ cm}^6 \text{ s}^2 \text{ photon}^{-2}$, which is three to four orders of magnitude higher than those of the previously reported common UV fluorescent dyes. © 2004 American Institute of Physics.
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Semiconductor nanocrystals have been receiving much attention in fluorescence microscopy and biology due to their attractive optical properties such as narrow emission bands, emission wavelength tunability with size, photostability, and enhanced brightness.¹ Recently, the two-photon excitation (2PE) technique has emerged as an invaluable tool for nanocrystal research, especially in identifying potential transitions between energy levels that are forbidden under one-photon excitation,² and in fluorescence imaging through thick biological samples.³ The two-photon absorption cross section of CdSe nanocrystals was predicted and measured to be approximately $\sim 10^{-46} \text{ cm}^4 \text{ s photon}^{-1}$, which is two to three orders of magnitude higher than the value of common fluorescent dyes.²

While 2PE has shown its valuable application in nanocrystals research, three-photon excitation (3PE) has never been applied to nanocrystal quantum dots. 3PE has several complementary advantages over 2PE. First, it can induce UV fluorescence such as nanocrystals CdS, ZnO, and GaN at the optimal wavelengths of commercial Ti:sapphire femtosecond lasers. Second, 3PE allows for the use of a long excitation wavelength and thus leads to a deep penetration depth in a thick sample. Lastly, the excitation wavelength of 3PE is separated further from the emission, which results in a better signal to noise ratio in imaging applications.

In this letter, the measured three-photon excited band edge and trap state emission of CdS nanocrystals is reported. In particular, the intensity dependence of band edge and trap state emissions on the incident power is investigated, which shows that the trap state emission is not dependent on the third power of the incident intensity, unlike the band edge emission. We also report on the measured three-photon ab-

sorption cross section for CdS nanocrystals and 3PE microscopy of CdS nanocrystals.

The CdS nanocrystals were prepared using chemical procedures developed recently by Yu and Peng.⁴ A mixture of cadmium oxide (0.256 g, 2 mmol), oleic acid (9.04 g, 32 mmol), and octadecene 70 g (Aldrich) was heated to 300 °C. A solution of sulfur (0.032 g, 0.5 mmol) in octadecene was swiftly injected into the reaction mixture and nanocrystal growth was continued at 250 °C and monitored spectroscopically. The nanocrystals were purified by repeated extraction of the reaction solution with methanol/chloroform (1:1). The purified CdS nanocrystals were dispersed in chloroform, and a droplet of the diluted sample was dried onto a coverslip for optical measurements.

The three-photon fluorescence of nanocrystals was excited with a titanium:sapphire ultrashort pulsed laser (Spectra-Physics Tsunami) operating at a pulse width of ~ 100 fs, a repetition rate of 80 MHz, and a wavelength range of 900–1000 nm. The multiphoton excited fluorescence from the focus of a high-numerical aperture objective lens (NA=1.45) was collected by the same objective, then refocused to a spectrometer with a CCD detector for spectrum acquisition and fluorescence photon counting or to a photomultiplier tube for imaging.⁵ We estimated our detection efficiency to be 0.005 counts per fluorescent photon emitted by the sample.

The fluorescence spectrum of CdS nanocrystals excited at 980 nm is shown in Fig. 1. The emission at 440 nm corresponds to the band edge emission and the broad emission at ~ 620 nm to the trap emission. As shown in Fig. 1(a), the band edge emission intensity depends on the third power of the incident power, demonstrating the 3PE fluorescence. However, unlike the band edge emission, the trap emission intensity dependence on power cannot be explained with such a power law, as Fig. 1(b) shows there is a deviation from a cubic power law. Such deviation of trap emission is

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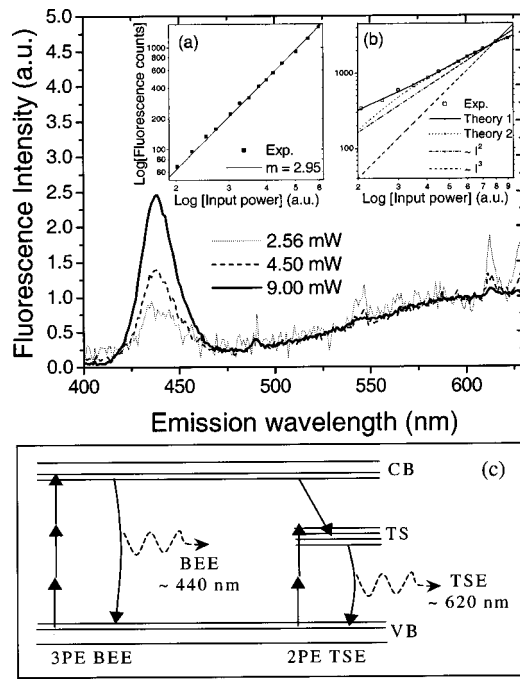


FIG. 1. Three-photon excited emission spectra of CdS nanocrystals. The emission spectrum at various excitation power was normalized to the trap emission peak (~ 620 nm). Due to the different emission intensity dependence on excitation power of the band edge (440 nm) and trap emissions, the relative strength between the two emission intensities changes with power. Inset (a) is the dependence of the band edge emission intensity of CdS nanocrystals on the incident power, showing the cubic dependence. Inset (b) is the dependence of the trap state emission intensity of CdS nanocrystals on the incident power. Theory 1: Eq. (2) with $n=2$; theory 2: Eq. (2) with $n=3$; $\sim I^2$: square law; $\sim I^3$: power-cubed law. Inset (c) is the energy diagram depicting 3PE of band edge emission, and direct 2PE of trap states. CB: conduction band; VB: valence band; TS: trap states; BEE: band edge emission; TSE: trap state emission.

believed to be caused by the limited number of trap states available within the nanocrystals. With the assumption of a single trap state level, the density of electrons in the trap states n_t can be expressed,⁶ as

$$\frac{dn_t}{dt} = \sigma_{rt} \alpha I^n (N_0 - n_t) - s n_t e^{-E_t/kT} - \sigma_{nr} n_t, \quad (1)$$

where σ_{rt} is the trap state capture cross section (either through conduction band or by direct absorption), σ_{nr} is the trap state nonradiative absorption cross section, I is the input intensity, N_0 is the trap state energy with respect to the conduction band edge, k is the Boltzmann's constant, T is the temperature, n is power index for an n -photon process, and α and s are constants. The first term of Eq. (1) represents the capture of carriers into the traps, the second term is the thermal excitation of electrons out of the trap, and the last term represent the nonradiative recombination from the trap. Solving for n_t gives

$$F \sim n_t = \frac{AI^n}{C + BI^n} [1 + \exp(-DI^n)], \quad (2)$$

where F is the fluorescence intensity, A , B , C , D are intensity independent functions, $A = \sigma_{rt} \alpha N_0$, $B = \sigma_{rt} \alpha$, $C = s \exp(-E_t/kT) + \sigma_{nr}$, and $D = \sigma_{rt} \alpha t$. In Fig. 1(b), we use Eq. (2) to fit the experimental values. Theory lines 1 and 2 are calculated using $n=2$ (2PE), and $n=3$ (3PE), respec-

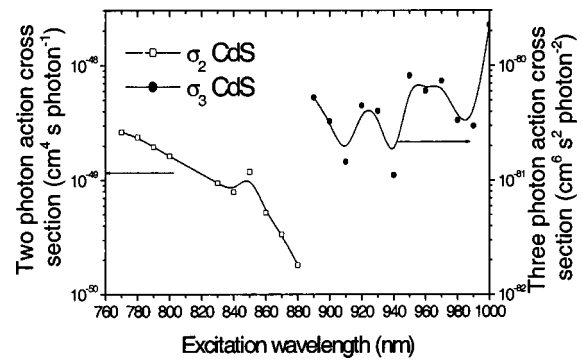


FIG. 2. Two- (770–890 nm) and three-photon (900–1000 nm) action cross sections of CdS nanocrystals.

tively. We have also shown the square law $\sim I^2$ and the cubic law $\sim I^3$ fits, which simply cannot adequately account for the observed data.

Although excitation wavelength at 980 nm implies that the band edge emission is due to 3PE, it is noted that *theory 1* fits more accurately to the experimental data than *theory 2*. *Theory 2* model deviates in the low power region (< 3 mW), suggesting that the trap emission is a 2PE process rather than a 3PE one. This is an unexpected result given that at the wavelength of 980 nm, only the 3PE band edge emission is possible and trap emission is usually excited via electrons relaxing from the conduction band. However, it is also possible that at 980 nm, the trap emission can be excited directly via two-photon excitation [electrons jumping directly to the trap states rather than through the conduction band, Fig. 1(c)]. To confirm this possibility, we have independently excited the nanocrystals with one photon at 488 nm, (cw Ar⁺ ion laser), in which only the trap emission at 620 nm is observed. Therefore, the trap emission can be excited directly by 2PE at a low power level. At high power levels, however, both the direct 2PE process and the 3PE process through the conduction band are expected. Indeed, above 3mW excitation power, both models fit the experimental data accurately.

To obtain the three-photon absorption cross section of CdS nanocrystals, we use^{7,8}

$$F \sim \eta \phi \sigma_3 N I^3, \quad (3)$$

where F is the fluorescence counts, η is the fluorescence quantum efficiency, ϕ is the fluorescence collection efficiency of the experimental system, σ_3 is the three-photon absorption cross section of CdS nanocrystals, N is the number of nanocrystals in the focal volume, and I is the incident intensity at the focus. Since the excitation beam was focused using a high numerical aperture objective (NA=1.45), we employed the vectorial Debye theory⁹ rather than the paraxial approximation theory⁷ in calculating the focal volume. The numerical calculation shows that the focal volume for NA=1.45 decreases more than 70% for 3PE case, when compared with NA=1.

The measured three-photon action cross section ($\eta_3 \sigma_3$) of CdS nanocrystals over the excitation wavelength range of 900–1000 nm is shown in Fig. 2. In the calculation, the collection efficiency ϕ was estimated to be $\sim 0.5\%$, and the number of nanocrystals N was estimated to be ~ 50 . In order to verify the accuracy of our measurements, we also mea-

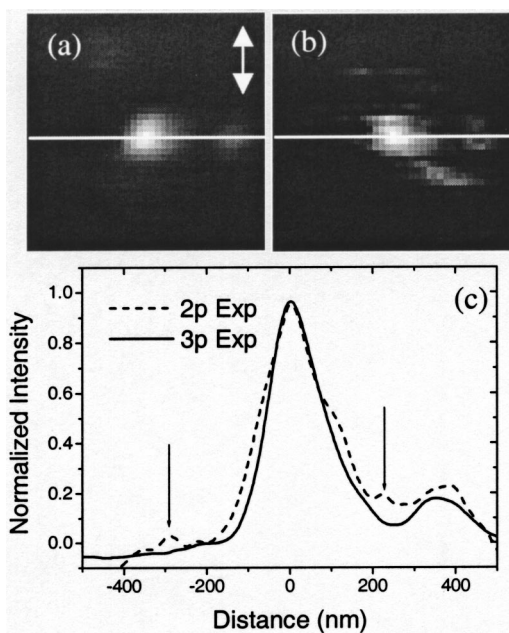


FIG. 3. Scanning images (PMT detection) of CdS nanocrystals excited by (a) three-photon (~ 1 MW/cm², 980 nm) and (b) two-photon (~ 0.2 MW/cm², 820 nm) absorption. The arrow indicates the direction of the incident polarization. (c) The cross section line plot of the images. The arrow indicates the difference in two-photon and three-photon excited images.

measured the two-photon action cross sections over the range of 770–890 nm. When calculating the absolute two-photon cross section, one needs to calculate the value of the quantum efficiency (η) at room temperature. The quantum efficiency is known to be highly dependent on temperature, and previous studies of the temperature dependence of photoluminescence of semiconductor nanocrystals^{6,10,11} have revealed that the luminescence decreases more than 100-fold when the temperature is increased from ~ 5 K to room temperature. Assuming such a dependence is also present in CdS nanocrystals, the absolute two-photon cross section is calculated to be $\sim 10^{-47}$ cm⁴ s photon⁻¹ at the excitation wavelength of 800 nm, which is close to the previously reported value for CdS.¹² From similar considerations, the absolute three-photon cross section for CdS nanocrystals is estimated to be of the order of $\sim 10^{-79}$ cm⁶ s² photon⁻², which is three to four orders of magnitude higher than the value of common UV fluorescent dyes.¹³

Generally, 3PE of nanocrystals provides better signal to background ratios than 2PE, because the intensity differences between the diffraction limited spot and the sidelobes are

cubed (3PE) rather than squared (2PE), therefore enhancing imaging contrast. Such an enhancement in contrast is shown in the microscopic images of CdS in Fig. 3, where the sidelobe-like feature is present (indicated by arrows) in the two-photon image but absent in the three-photon image [Fig. 3(c)]. Further, a smaller full width at half maximum (i.e., transverse resolution) for 3PE was observed in the direction perpendicular to the incident polarization. The slight elongation toward the incident polarization direction is due to the depolarization effect of a high numerical-aperture objective.⁵

In conclusion, the 3PE band edge and trap emission of nanocrystals have been measured. It has been shown that the dependence of the band edge emission on the excitation intensity closely follows the cubic power law, demonstrating 3PE, but the trap emission intensity does not follow such a dependence. A simple theoretical model with a single trap state shows good agreement with experiment, indicating the trap emission saturation could be caused by the limited trap density of states. We have also measured the three photon absorption cross section of the CdS nanocrystals, and found it to be three to four orders of magnitude higher than those of dye molecules. Semiconductor nanocrystals with such high three-photon absorption cross section values will prove to be extremely useful biological fluorescent labels, potentially replacing UV fluorescent dyes.

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