

Fluorescence Enhancement of CdSe Q-Dots with Intense Femtosecond Laser Irradiation

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Abstract Effects of intense femtosecond (fs) laser irradiation on the optical properties of cadmium selenide (CdSe) nanocrystals are studied. We present the changes in emission and absorption of laser (800 nm, 110 fs, Ti-Sapphire) irradiated CdSe nanocrystals dispersed in dimethylformamide (DMF). It is observed that the absorbance of CdSe nanocrystals capped with trioctylphosphine (TOP) increases with the number of laser pulses. The trap state luminescence intensity of these crystals degrades, whereas the band edge luminescence intensity shows an increase as a function of the fs laser irradiation. We also report strong two photon absorption and reduction in the trap state luminescence intensity after irradiation with the laser pulses.

Keywords Cadmium selenide nanocrystals · Band edge emission · Trap state emission · Two photon excited fluorescence

Introduction

In recent years, interest in the synthesis, characterization, and application of colloidal “quantum dot” semiconductor materials has grown markedly [1]. Nanocrystals of CdSe are by far the most studied system among all the semiconducting nanocrystals. Colloidal quantum dots (QDs), also known as semiconductor nanocrystals, are synthesized by chemical routes and dispersed in suitable solutions. Nanocrystals smaller than the Bohr radius of the particular

semiconductor demonstrate unique optical properties due to the effects of three dimensional quantum confinement. Smaller the crystal, greater is the confinement potential (roughly corresponding to particle in a spherical box); this results in a broadening of the band gap that is inversely proportional to the particle size. The bulk CdSe has a direct band gap of 1.74 eV at 300 K, and the typical Bohr exciton diameter of CdSe is around 10.6 nm; consequently, CdSe nanocrystals in the size of <11 nm show sizable quantum confinement effects with remarkably different optical properties. The changes in the properties of nanocrystals are driven mainly by two factors, namely the increase in the surface to volume ratio, and drastic changes in the electronic structure of the material due to quantum mechanical effects with decreasing crystal size.

In the QDs, photoluminescence occurs when an electron is excited into the conduction band levels, creating an electron-hole pair which recombines to emit a photon. The broader the band gap, more energetic is the photon and hence bluer will be the emission wavelength. Depending upon the material, QDs can be tuned to emit at different visible or infrared wavelengths by controlling their sizes [2]. QDs have several proven and potential applications as biosensors; these are used as fluorescent dyes [3–9] in sensor applications. These inorganic dyes have great advantages over conventional organic dyes; such advantages include the option for continuously and precisely tuning the emission wavelength of QDs by changing the size of the nanocrystals, narrow symmetric emission spectra, a single light source can be used for simultaneous excitation of multiple semiconductor quantum dots with different emission spectra, ability to function through repeated cycles of excitation and fluorescence for hours and extreme stability of coated quantum dots against photobleaching as well as changes in the pH of the biological

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electrolytes that are ubiquitous in biological environments. These novel optical properties render QDs ideal fluorophores for ultrasensitive, multicolor, and multiplexing applications in cell and molecular biology as well as in bioengineering.

Nevertheless, these nanocrystals have some limits for special applications. First, the photoluminescence intensity initially increases on continuous excitation and converges to a maximum value. This effect is well-known in solid-state physics and can be attributed to traps (surface, intrinsic, impurities, etc.) in the nanocrystals. Competition between band-edge luminescence and alternative decay paths over traps occurs under continuous excitation. The traps are saturated gradually, and band-edge luminescence is preferred [10]. When all the traps are saturated or there is equilibrium between band-edge luminescence and other forms of recombination, the luminescence remains constant. To make sensitive and sharp fluorescent QDs, these trap states should be controlled. Recently many reports have come on preparation and surface modifications of nanocrystals with laser beam [11–13]. Femtosecond pulsed lasers have been widely used in structure modification of materials. Because of its high peak intensity, these lasers are useful in the surface modifications of the materials. These ultra short laser pulses induce low thermal changes and the wavelength (800 nm) used is far from the bandgap of the CdSe nanocrystals which prevents agglomeration or physical damage of the nanocrystals. In our present studies 800 nm, 110 fs Ti/sapphire laser irradiation is used to modify the surface of the CdSe nanocrystals so that trap state emission is reduced and band edge emission is improved. The band edge emission spectra of QDs are narrow; hence a single sample may be labeled with many probes. Improvement in the band edge emission is therefore more helpful in biological applications.

Experiments

CdSe nanocrystals are prepared by chemical methods. The precursors used: 2.35 g of cadmium acetate dihydrate, 0.5 g of selenium, and 1 ml of TOP added to 5 ml of DMF, are heated at 110°C for 1 h under nitrogen atmosphere. Following this, the yellowish TOP capped CdSe nanocrystals obtained are washed with acetone and ether. The synthesized nanocrystals are irradiated with 800 nm, 110 fs, 1,000 Hz, 8.03 MW cm⁻² (8 mm beam diameter) wavelength, pulse width, repetition rate and peak intensity of laser beam respectively. The size measurements and surface morphology of the CdSe nanocrystals are carried out by powder XRD (INEL X-Ray diffraction spectrometer with Co target) and transmission electron microscope (TEM) studies. The TEM pictures are taken on carbon

coated copper grids with JEOL (JEM 2100) system at 100 KV and 58 iA. The UV/VIS absorption spectrum of the nanocrystals are recorded at room temperature with a spectrophotometer (Shimadzu 3101PC), the photoluminescence properties of these nanocrystals are studied with the fluorescence spectrometer (Jobin Yvon Horiba FluoroMax-3) and the two photon excited fluorescence spectra excited with 800 nm, 110 fs pulses (Spectra-Physics, Maitai-Spitfire), collected with Ocean Optics spectrometer (USB 2000). Emission and absorption properties of the irradiated CdSe nanocrystals show interesting behavior with increase in the number of the laser pulses irradiating the sample.

Results and discussion

The synthesized CdSe nanocrystals were dispersed in DMF for our studies; which forms a clear yellowish colloidal solution. From the XRD spectra of CdSe, as shown in Fig. 1, it is very evident that the nanostructures formed are crystalline in nature. The (h k l) planes obtained from the spectra are (1 0 0), (1 1 0), and (1 1 1). The crystal size (D) is calculated using the Scherer formula [14], $D = (0.9 \lambda / (B \cos \theta))$, where λ is the wavelength of the X-radiation, B is the full width at half maximum (FWHM) of the XRD peak, and θ is the half of the Bragg angle at maximum peak height. There is no modification in the XRD spectrum after fs laser irradiation. Though one could get a rough estimate of the average grain size using the XRD data, a better estimate of the crystal size is obtained by TEM studies. The TEM pictures of the CdSe nanocrystals are shown in Fig. 2. The monodispersity of nanocrystals in DMF is very evident from the Fig. 2 indicating that the nanocrystals are well separated from each other. The TEM picture of CdSe

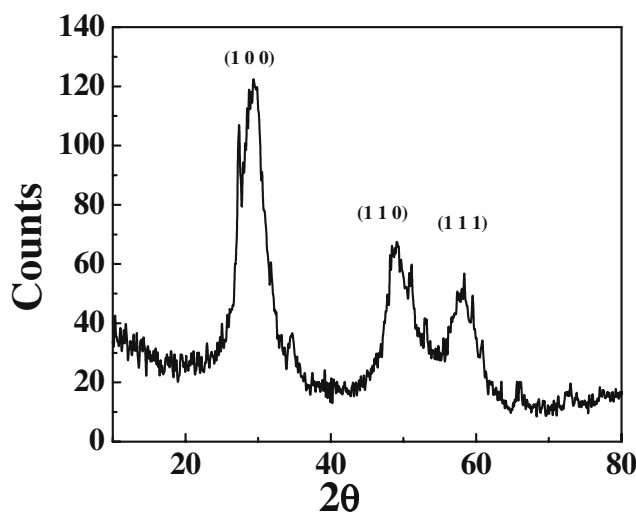
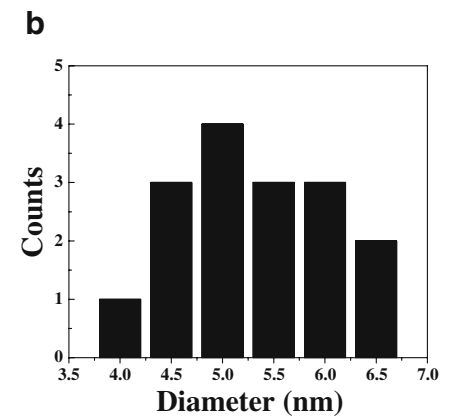
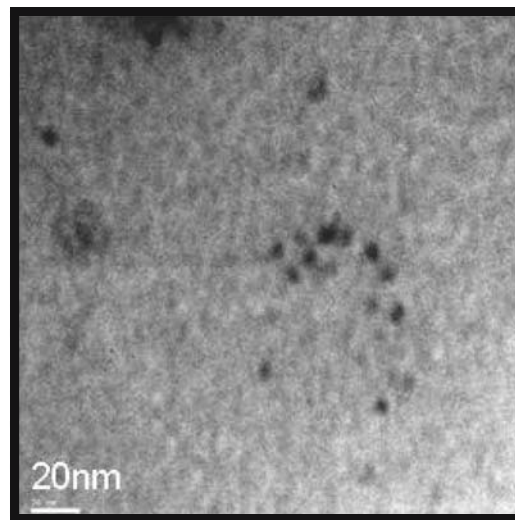
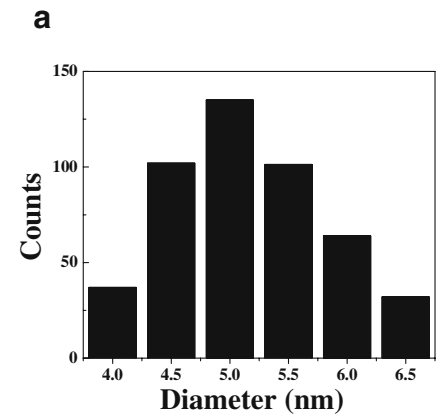
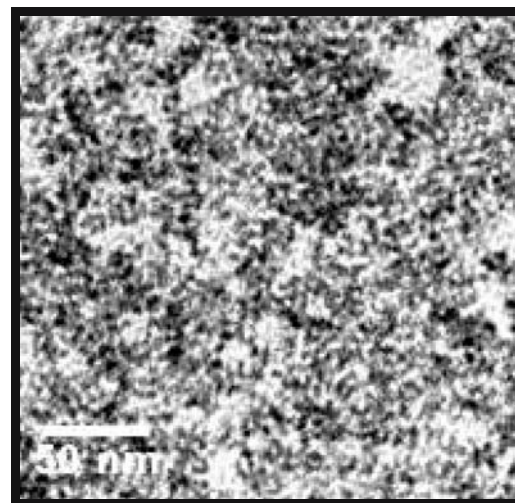


Fig. 1 X-Ray diffraction of CdSe Q-Dots

Fig. 2 **a** TEM picture of CdSe nanoparticles before fs laser irradiation, **b** TEM picture of CdSe nanocrystals after 35,000 fs laser pulses irradiation



nanocrystals before and after fs laser irradiation (35000 pulses) are shown in Fig. 2a and b respectively. The average crystal size is measured to be 5.4 nm in both cases, which clearly shows that the size of nanocrystals remains the same even after irradiation with fs laser pulses.

The UV/VIS absorption spectrum of the nanocrystals after irradiation with different numbers of laser pulses is shown in Fig. 3. This clearly shows an increase in the absorption intensity with the number of pulses irradiating the sample. Figure 3 also shows sharp absorption peaks at 328 nm and exciton peak at 475 nm. The emission properties of these nanocrystals are also studied with the excitation of 328 and 475 nm. The luminescence property of these nanocrystals exciting at 475 nm is shown in Fig. 4, which shows a broad peak at 705 nm and a sharp peak at 523 nm. The 523 nm emission is the band edge emission peak, which is close to the excitation wavelength, while the broad emission peak at 705 nm is contributed by the presence of trap states [15, 16]. The deep trap states are

mostly due to the surface ions. In our studies, we observed that with irradiation the trap state emission degrades and band edge emission improves. This is also confirmed by 328 nm excited luminescence spectra shown in Fig. 5, which is mainly due to the emission from band edge levels. The two photon excited fluorescence spectra of CdSe nanocrystals excited with 800 nm, 110 fs pulses is shown in Fig. 6, where CdSe nanocrystals absorb two photons of 800 nm to go to the conduction band levels and emit a single photon of wavelength 703 nm, which is a trap state emission. The trap states are mostly due to ions located on the surface with Cd^{+2} or Se^{-2} deficiency. Due to fs laser irradiation surface atoms reorganize to form CdSe and thereby leading to reduction in the trap states with laser irradiation, which is evident from the reduction in the luminescence intensity due to the trap states as seen in Fig. 4. However this process saturates at a particular stage. The increase in the absorption intensity with number of laser pulses used for irradiation can be attributed to the

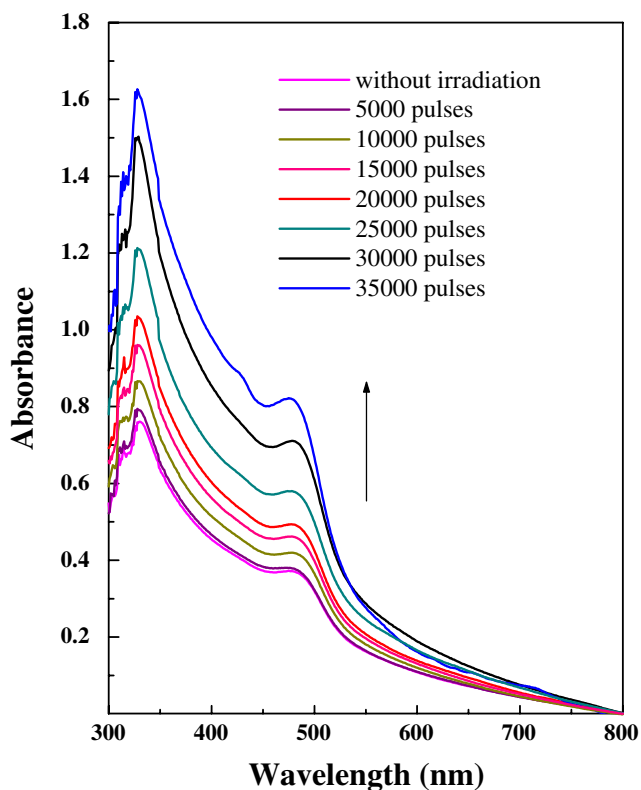


Fig. 3 Absorption spectra of CdSe nanocrystals irradiated with different numbers of laser pulses

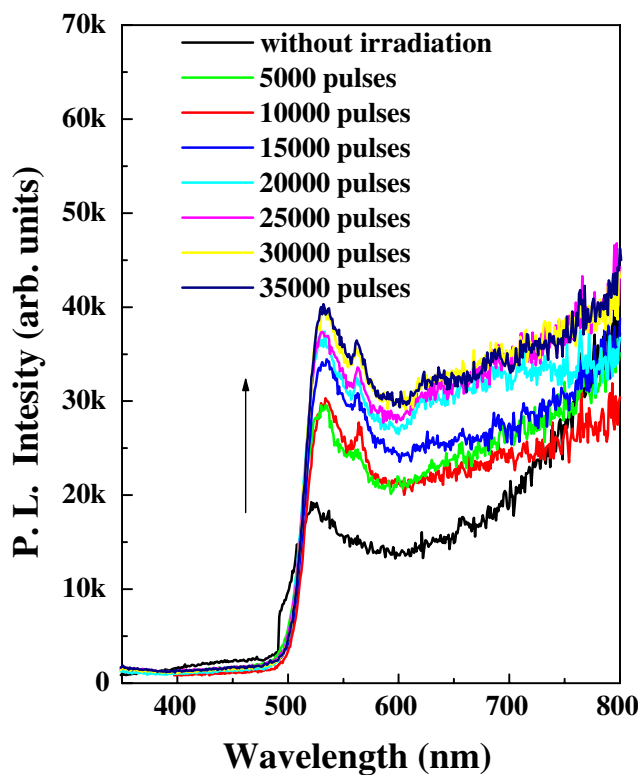


Fig. 5 Emission spectra of CdSe nanocrystals irradiated with different numbers of laser pulses, excited at 328 nm

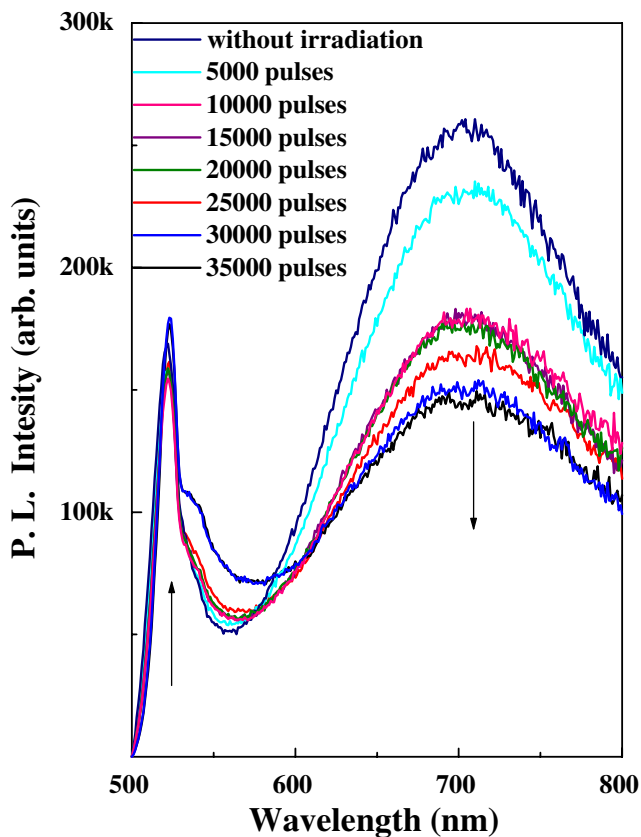


Fig. 4 Emission spectra of CdSe nanocrystals irradiated with different numbers of laser pulses, excited at 475 nm

formation of CdSe molecules. The decrease in the number of surface ions leads to degradation in the trap state emission intensity and hence an improvement of the band edge emission intensity.

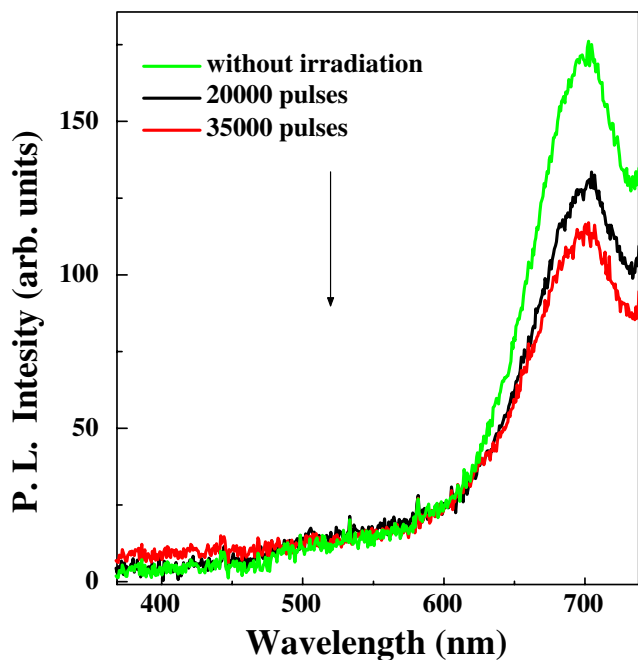


Fig. 6 Emission spectra of CdSe nanocrystals irradiated with different numbers of laser pulses, excited at 800 nm, 110 fs laser

Conclusion

Femtosecond laser beam irradiation is one of the best methods to modify the surface of the nanocrystals leading to changes in absorption and luminescence properties without changing the size of nanocrystals. Our results show significant degradation in the trap state luminescence and improvement in the band edge luminescence from the nanocrystals after fs laser beam irradiation. These changes depend on the number of laser pulses irradiating the sample and it is mainly due to decrease in the number of surface ions of the nanocrystals. Improvement in the band edge emission is a good signature for CdSe nanocrystals in biological applications.

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References

- Alivisatos AP (1996) Perspectives on the physical chemistry of semiconductor nanocrystals. *J Phys Chem* 100:13226–13239
- Dabbousi BO, Rodriguez-Viejo J, Mikulec FV, Heine JR, Mattoussi H, Ober R, Jensen KF, Bawendi MG (1997) (CdSe) ZnS core-shell quantum dots: synthesis and characterization of a size series of highly luminescent nanocrystallites. *J Phys Chem B* 101:9463–9575
- Bruchez M, Moronne M, Gin P, Weiss S, Alivisatos AP (1998) Semiconductor nanocrystals as fluorescent biological labels. *Science* 281:2013–2016
- Han M, Gao X, Su JZ, Nie S (2001) Quantum-dot-tagged microbeads for multiplexed optical coding of biomolecules. *Nat Biotechnol* 19:631–635
- Jaiswal JK, Mattoussi H, Mauro JM, Simon SM (2003) Long-term multiple color imaging of live cells using quantum dot bioconjugates. *Nat Biotechnol* 21:47–51
- Leatherdale CA, Bawendi MG (2001) Observation of solvatochromism in CdSe colloidal quantum dots. *Phys Rev B* 63:165315–165321
- Zhang P (2006) Investigation of novel quantum dots/proteins/cellulose bioconjugate using NSOM and fluorescence. *J Fluoresc* 16(3):349–353
- Liu T, Liu B, Zhang H, Wang Y (2005) The fluorescence bioassay platforms on quantum dots nanoparticles. *J Fluoresc* 15(5):729–733
- Zahavy E, Freeman E, Lustig S, Keysary A, Yitzhaki S (2005) Double labeling and simultaneous detection of B and T cells using fluorescent nano-crystal (q-dots) in paraffin-embedded tissues. *J Fluoresc* 15(5):661–665
- Riegler J, Nann T (2004) Application of luminescent nanocrystals as labels for biological molecules. *Anal Bioanal Chem* 379:913–919
- Zeng H, Qiu J, Jiang X, Zhu C, Gan F (2004) The effect of femtosecond laser irradiation conditions on precipitation of silver nanoparticles in silicate glasses. *J Phys Condens Mater* 16:2901–2906
- Pereiral A, Cros A, Delaporte P, Georgiou S, Manousaki A, Marine W, Sentis M (2004) Surface nanostructuring of metals by laser irradiation: effects of pulse duration, wavelength and gas atmosphere. *Appl Phys A* 79:1433–1437
- Masuo K, Plaksin OA, Fudamoto Y, Okubo N, Takeda Y, Kishimoto N (2006) Effects of laser irradiation on nanoparticle evolution in SiO₂ implanted with Cu ions. *Nucl Instrum Methods Phys Res B* 247:268–270
- Cullity BD (1977) *Elements of X-ray diffraction*. Addison-Wesley, New York
- Venkatram N, Sai Santosh Kumar R, Narayana Rao D (2006) Nonlinear absorption and scattering properties of cadmium sulphide nanocrystals with its application as a potential optical limiter. *J Appl Phys* 100:074309-1-074309-8
- Kuno M, Lee JK, Dabbousi BO, Mikulec FV, Bawendi MG (1997) The band edge luminescence of surface modified CdSe nanocrystallites: probing the luminescing state. *J Chem Phys* 106(23):9869–9882