PHYSICS, CHEMISTRY AND APPLICATION OF NANOSTRUCTURES, 1999

# EFFECT OF SELF-DEFOCUSING IN THIN FILMS OF CLOSE-PACKED CdS NANOCRYSTALS

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**The thin solid films of CdS nanocrystals on quartz substrate were produced and their nonlinear response were studied by Z-scan method using $Ar^+$ laser. The magnitude and sign of the nonlinear refractive index $n_2$ were determined.**

CdS nanocrystals were synthesized by the reaction between $10^{-3}$ M solution of Cd-thioglycerol complex and $10^{-3}$ M $Na_2S$ in dimethylsulfoxide (DMSO) at room temperature. Residual ions were removed by precipitating nanocrystals with acetone and redissolving in a fresh portion of DMSO. The fast mixing of these solutions results in creation of colloidal CdS nanocrystals, surface captured by thioglycerole monolayer. This surface monolayer prevents CdS nanocrystals from recrystallization giving ultrasmall highly monodisperse colloidal particles. Thin films of close packed CdS nanocrystals were obtained by centrifugation of nanocrystals onto a quartz glass plate from DMSO/acetone 1:1 mixture.

The transmission spectra of the samples were measured using a Shimadzu UV-360 spectrometer at room temperature in the wavelength range of 250-2700 nm. The measurements indicated a transmittance of 92 % at the 514.5 nm wavelength used in the subsequent Z-scan measurements. The data obtained from the transmission spectra were used also for determination of the film thickness (L=588±14 nm) by the fitting procedure described in [1]. The absorption spectra of thin film of CdS nanocrystals (Fig. 1) show the strong excitonic transition at 3.75 eV, which reveals the strong effect of quantum confinement in such nanocrystals. The average particle size of 1.6-1.8 nm was evaluated from the data of small angle X-ray diffraction analysis. This is twice less than the Bohr radius of bulk CdS exciton.

Z-scan experiments were performed with a continuous-wave $Ar^+$ laser operating at 514.5 nm. The experimental setup is shown schematically in Fig. 2. The laser beam of Gaussian temporal and spatial profile was focused using a 62 mm focal length lens. The radius at the beam waist was 25 μm. For the Z-scan measurements, the sample was translated along the optical axis of the beam. The laser beam

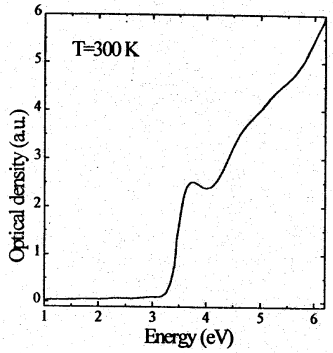


**Figure 1.** Optical absorption spectrum of the film of CdS nanocrystals.

profile was recorded as a function of the sample position Z with the use of CCD camera in the far field. Measurements were carried out over the laser power region of 75÷250 mW.

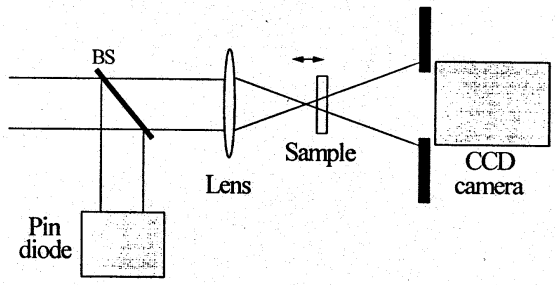


**Figure 2.** Z-scan experimental apparatus.

The experimental data for the laser power of 250 mW are displayed by solid squares in Fig. 3. For calculations of the transmission we define the irradiance by

$$I(r) \propto I_p \exp\left(-\frac{r^2}{r_0^2}\right),$$

where $I_p$ is the peak irradiance, $r^2 = x^2 + y^2$, and $r_0$ is the half-width of the beam profile at $e^{-1}$ of the maximum, x and y are the point Cartesian coordinates in the transversal direction. The transmission was normalised with the data obtained at large values of Z.

The signal profile with a peak followed by a valley is know to be the indicative of a negative (self-defocusing) optical nonlinearity. The nonlinear refractive index, $n_2$, can be evaluated using the measured difference in the peak-to-valley normalised

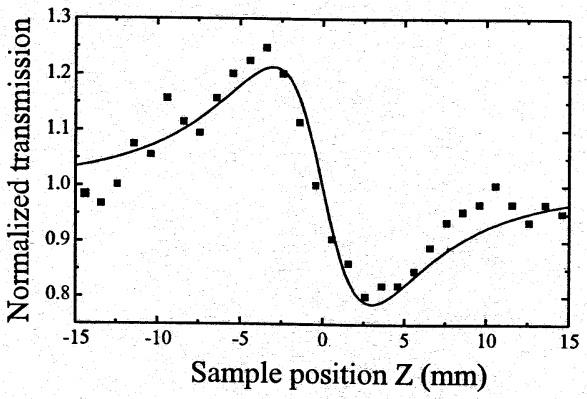


**Figure 3.** Laser beam normalized transmittance versus the sample position. Incident average power is 250 mW.

transmittance, $\Delta T_{p-v}$, corresponding to small aperture [2]

$$n_2 = \frac{\lambda}{2\pi L_{eff}} \frac{\Delta T_{p-v}}{0.406\,(1-S)^{0.25} I_0},$$

where S (0.01) is the linear transmission of the aperture, $\lambda$ is the laser emission wavelength, $L_{eff} = [1-\exp(-\alpha \cdot L)]/\alpha$ is the effective sample length, $I_0$ is the intensity of the laser beam at focus, and $\alpha$ is the linear absorption coefficient. The value of $\Delta T_{p-v}$ was obtained through the theoretical fit from the results of Z-scan measurements using procedures described in [2]. The solid line in Fig. 3 is the result calculated using the phase distortion value $|\Delta\Phi| = 1.05$, which gives the absolute value of the nonlinear refractive index of $1.8 \cdot 10^{-6}$ cm$^2$/W.

In the general case the nonlinear response of nanocrystals may be contributed by electron-hole pairs, trapping states, and thermal effects [3]. It is tempting to relate our results to thermally induced nonlinear effects for the following reasons. (1) The continuous-wave laser beam was used in our experiments instead of a short pulses beam which can reduce heat effect to the minimum. It is well known that the thermal relaxation time of the semiconductor-doped glasses may be as great as 1 ms, whereas the electronic relaxation occurs in time interval $\leq$ 10 μs [4]. Unfortunately, little is known at the present time about the laser-induced temperature effects in films of close-packed nanocrystals. (2) The peak-to-valley configuration of the Z-scan trace in Fig. 3 indicates a self-defocusing nonlinearity ($n_2 < 0$), which may be assigned (at the indicated conditions) to laser heating processes. (3) The possibility of the heat transfer from thin absorbing film of nanocrystals to quartz substrate must not be ruled out. This process also can induce nonlinear effects in substrate, especially, at sufficiently large value of the absorption coefficient of the film.

The obtained results, however, may be interpreted as arising from nonthermal effects. In the bulk semiconductor, a heating affects the optical nonlinearity through the mechanism of energy band distortion. However, in the semiconductor nanoparticles, the energy band is splitted into a series of discrete levels due to the confinement effect, and the confined kinetic energy is much greater than the thermal one [5]. In such situation, other mechanisms play major role in the enhancement of optical nonlinearity of close-packed CdS nanocrystals. (1) The surface-trapped states could also significantly contribute to the optical nonlinearity with a large and slow response [6]. The direct excitation of these states will generate photocarriers which will also give a negative nonlinear $n_2$. (2) The optical Stark effect of the nanoparticles can be enhanced through charge separation of the core/surface structure [7]. (3) The excitation of nanoparticles at the laser wavelength in our experiment satisfies the condition $E_g/2 < \hbar\omega < E_g$, hence, the two-phonon absorption can take place and transmittance may be affected by both the nonlinear refraction and absorption.

To the authors' knowledge, the value of the nonlinear refractive index which was obtained in this work is many times higher than the value reported previously for CdS nanocrystals embedded into different matrices. Taking into account the extremely high volume concentration of close-packed nanocrystals in the films, this result agrees well with the observed dependence of the optical susceptibility on volume factor of nanoparticles in the matrix [8].

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Minsk, Belarus 17—21 May 1999


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