GROWTH OF FREE AND TRAPPED EXCITON LUMINESCENCE OF QUANTUM-SIZED CdS NANOCRYSTALS UNDER COMBINED UV LASER IRRADIATION AND STATIC ELECTRIC FIELD ACTION

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Extremely small size and high surface-to-volume ratio of quantum-confined semiconductor nanoparticles condition the strong influence of surface states onto their optical properties. Since the wavefunctions of excited electron-hole pairs in quantum-sized (QS) nanocrystals extend to the particle surface, both the electrons and holes can be easily captured by adsorbed molecules resulting in the pronounced photochemical degradation of QS particles, change in luminescence quantum yield etc. [1-2]. The well-exciton photoluminescence (PL) of QS CdS, CdSe nanocrystals in glass matrix during the prolonged UV irradiation is attributed to irreversible electron capture in glass [3-4].

In this work we observed the photoinduced as well as dc electric field assisted enhancement of free and trapped exciton PL bands in QS CdS nanocrystals in polyvinylpyrrolidone (PVP) film. The QS CdS nanoparticles were synthesized in usual way [5] by chemical reaction between cadmium acetate (10^{-3} M) and H_2S ($\approx 5 \cdot 10^{-3}$ M) both dissolved in dry methanol. The small amount ca. 2 % of PVP was added to methanolic solution as the polymer-stabilizer of nanoparticles formed. The colloidal solution of QS CdS nanoparticles was placed onto quartz glass covered by transparent

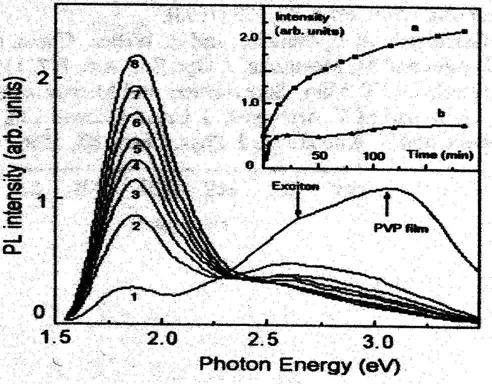

Fig. 1.
PL spectra of QS CdS nanocrystals in PVP film during the prolonged irradiation by cw He-Cd laser (λ=325 nm) of various time duration, min: 1 - 0; 2 - 14; 3 - 28; 4 - 42; 5 - 56; 6 - 84; 7 - 116; 8 - 186. Insert: the kinetics of trapped (a) and free excitonic (b) PL bands during the irradiation.

conductive SnO_2 film (ρ = 5 kOhm cm^{-1}) and dried until a PVP film with CdS nanoparticles has formed. The luminescence experiment was carried out with cw He-Cd laser (λ = 325 nm, 3 mW output) as excitation source and commercial computer-controlling photoluminescence spectrometer. The capacitor structure was used to study the influence of static electric field on PL spectra, where the SnO_2 film with QS CdS nanocrystals in PVP matrix served as one electrode and thin copper foil separated from SnO_2 film by 1 mm spacer as second one.

Fig. 1 shows the substantial growth of trapped exciton PL band at E=1.88 eV and less pronounced increase in intensity of free exciton PL band at E=2.58 eV masked by luminescence from PVP film during the prolonged irradiation by He-Cd laser. The PL from PVP matrix degrades fastly so, that PL intensity at E=2.58 eV of pure PVP film was substrated from the same of PVP film with QS CdS particles giving us the pure dynamics of enhancement of free exciton PL band during prolonged irradiation (see insert in Fig. 1).

Fig. 2 shows the growth in intensity of trapped exciton PL band vs irradiation time with two 60 min dark pauses. The reversibility of photoinduced enhancement in PL intensity can be concluded.

Fig. 3 shows the combined action of UV laser irradiation and applied dc electric field on intensity of trapped exciton PL band. The applied electric field causes the increase in saturation PL intensity both when it is switched on at the beginning (t=0) of prolonged irradiation (curve 1) and after the t=120 min (curve 2). Fig. 3 clearly shows the photo- and electric field-induced enhancement of exciton PL intensity relates to the identical mechanism. Since the oxygen adsorbed at the semiconductor surface normally quenches both the free and trapped PL in QS nanocrystals [6] we propose the mechanism of photo- or electric field-induced desorption of oxygen from the surface of our QS CdS particles. The rigid polymeric film retards the diffusion of desorbed oxygen far from the CdS nanocrystals and the reverse adsorption process takes place within a minutes.

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Fig. 3.
The growth of intensity of trapped exciton PL band ($E=1.88$ eV) of QS CdS nanocrystals in the presence of static electric field of $9.5 \cdot 10^3$ V cm^{-1} switched on at $t=0$ (1) and 120 (2) min after the start of prolonged irradiation by He-Cd laser.

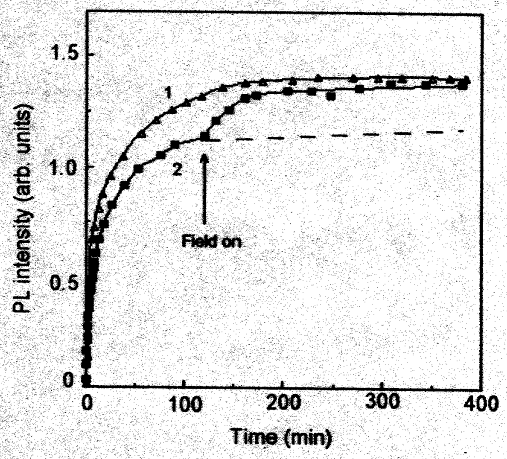

Fig. 2.
The kinetics of trapped exciton PL band ($E=1.88$ eV) of QS CdS nanocrystals during the irradiation by He-Cd laser with two 60 min dark pauses.