Luminescence of CdS quantum dots	Sự phát quang của các chấm lượng tử CdS checked 2
Abstract. The luminescence	Tóm tắt. Chúng tôi tiến hành

spectra of CdS nanocrystals (NC), or the quantum dots, dispersed in SiO2 porous matrix were carried out in different temperatures and under different excitation power. The photoluminescence (PL) exhibits the ranges, which relate to exciton levels, defect levels or shallow surface trap levels in CdS nanoparticles. Temperature dependence of PL intensity of CdS nanocrystals shows the thermal quenching of luminescence, this thermal quenching originates from the thermal ionization of electrons or holes trapped on surface defects of CdS nanocrystals and the thermal activation of excitons localized at the surface of nanocrystals with surface fluctuation. Two bands in photoluminescence excitation (PLE) spectra with various detective energies are observed. There is a band maximum at 370nm in all spectra. The decay times of photo-excited carriers in CdS NCs in xerogel and silica host matrix were investigated. The lifetime of CdS NCs is very short which inferior nanoseconds.

Experimental spectra show the presence of the quantum

nghiên cứu phổ phát quang của các tinh thể nano CdS (NC), hoặc các chấm lượng tử, phân tán trong nền xốp SiO2 trong các điều kiện nhiệt độ và công suất kích thích khác nhau. Phổ quang phát quang là các dải phổ tương ứng với các mức exciton, các mức sai hỏng hoặc các mức bẫy bề mặt nông trong các hạt nano CdS. Sự phụ thuộc nhiệt độ của cường độ PL của các tinh thể nano CdS thể hiện ==hiệu ứng dập tắt quang do nhiệt==, hiệu ứng dập tắt do nhiệt này bắt nguồn từ sự ion hóa nhiệt của các electron và lỗ trống bị bẫy trên các sai hỏng bề mặt của các tinh thể nano CdS và sự kích thích nhiệt các exciton định xứ ở bề mặt của các tinh thể nano với (có) dao động bề mặt. Hai dải phổ kích thích quang phát quang (PLE) ứng với các năng lượng phát hiện khác nhau cũng xuất hiện. Có một dải có cực đại ở 370 nm trong tất cả các phổ. Chúng tôi cũng nghiên cứu thời gian phân rã của các hạt tải kích thích quang trong các tinh thể nano CdS trong nền vật liệu chủ xerogel và silic điôxit. Thời gian sống của các tinh thể nano CdS rất ngắn, ngắn hơn nano giây.

Phổ thực nghiệm cho thấy sự hiện diện của hiệu ứng giam

confinement effect into small CdS dots.

INTRODUCTION

In the last years, growing interests have been put into semiconductor nanoparticles (quantum dots) because of their potential applications in the areas of solar energy conversion, photocatalysis and the optoelectronics and microelectronics industry due to their size – dependent optical properties [1, 2, 3, 4]. Among semiconductor quantum dots, cadmium sulfide (CdS) nanocrystals doped in silica glasses have been of great interest because of their band gap corresponds to the visible region of the electromagnetic spectrum and of the their giant nonlinear optical coefficients.

There are deferent investigations on some aspects of the optical properties of the CdS nanocrystals, which grows in deferent matrix. In this paper we report on the photoluminescent (PL) spectroscopy of CdS nanocrystals, which dispersed in the porous silica glass matrix. We investigate the influence of quantum size effect to optical properties of CdS nanocrystals; the temperature dependence and

cầm lượng tử trong các chấm lượng tử CdS nhỏ.

excitation energy of photoluminescence of these nanocrystals. The dynamics of PL of the samples was considered.

EXPERIMENTAL

CdS dots dispersed in SiO2 porous matrix were prepared by mixing a colloidal solution of CdS quantum dots (doping solution) with a matrix sol of polymerizable silanes, using procedure similar to that reported in Ref. [5,6,7]. The used chemical substances are CH3 CSNH2; CH3 CSNH2; tetraethoxysilane (TEOS) or methyltriethoxysilane (MTES) and the solvents as methanol (CH3OH); ethanol (CH3CH2OH) and a 3-mercaptopropyltrimethoxysilane (MPTMS) as surfactant agent. The details of the process to prepare CdS nanocrystals dispersed in SiO2 porous matrix were expounded in [8, 9]. The obtained samples are yellow transparent glasses.

The structure of CdS NCs dispersed in the bulk xerogels and mesoporous silica glasses were characterized by X - ray diffraction (XRD) using Siemen D-5000 diffractometer operating. The Raman scattering at room temperature was performed with the 488 nm line Ar+

laser excitation by Micro-Raman (Labram 1B) of Jobin-Yvon. Optical absorption spectra of CdS samples are performed in the region 350-550 nm wavelengths.

Photoluminescence (PL) spectra under pulsed 337.1 nm excitation at various temperatures from 300K to 77K. PL and photoluminescence excitation (PLE) spectra under continuous excitation of Xenon lamp were taken at defferent temperatures with a Jobin-Yvon Spectrometer HR460. The PL decays were analyzed by a PM Hamamatsu R5600U and a scope Tektronix TDS 784A with a time constant of the order of 1 ns and by a PM Hamamatsu R928 and a scope Nicolet 400 with a time constant of the order of 10 ns.

RESULTS AND DISCUSSION

In comparing with JCPDS-ICDD data, the X-ray diffraction (XRD) patterns show the presence of two crystallite phases of hexagonal wurtzite CdS and cubic CdS in the all samples. The similar case of crystal structure (hexagonal and/or cubic) could not be assigned with certainty as reported in

[6]. The broadening of the group of diffraction peaks in the range from 22 to 300 can be attributed to the very small size of CdS nanocrystals in the samples.

The resonance Raman scattering was performed to characterize the CdS quantum dots (Fig.1). The asymmetric broadening and the shift of the peak position of the LO-phonon energy to lower-frequency in comparison with CdS bulk was observed by using the excitation laser at 2.54 eV. This

Fig.1: The Raman spectra for CdS nano crystals (curve 1) and CdS bulk (curve 2)

Fig.2: The absorption spectra of the samples with 1%; 2 % and 10 % CdS nanocrystals (curve 1; 2 and 3, respectively); the narrow indicates absorption edges of bulk CdS crystal

Asymmetric broadening and small shift of the peak energies in the Raman spectrum present the contributions from the surface optical modes and this is related to quantum confinement of phonons into small CdS dots. Further, the resonance Raman scattering of CdS quantum dots shows the change of the ratio
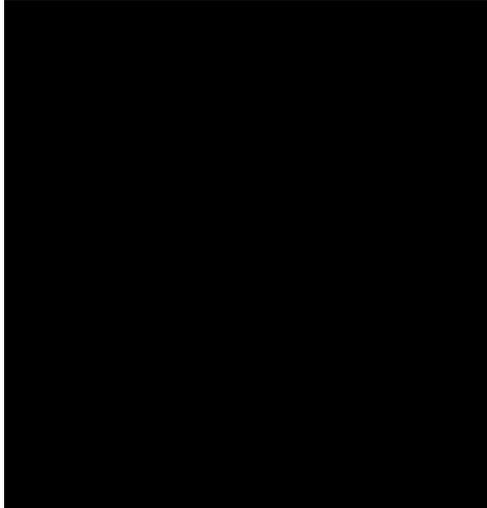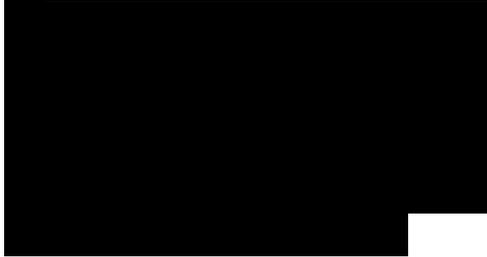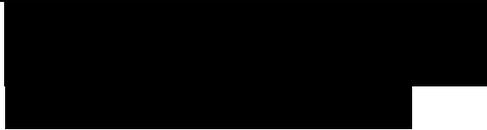
between the zero- phonon integrated intensity and their phonon replicas. This ratio is a function of NC sizes as reported in [10] In the simplest picture of nanocrystal electronic states, quantum confinement of the exciton lead to enhanced electron – hole overlap and reduced electron – phonon [10]. This results in the zero-phonon integrated intensity increases while the integrated intensity phonon replicas decreases. This change presents the confinement effect in the semiconductor quantum dots with nanometer size.

To estimate the effective bangap Eg(R) in the CdS quantum dots with radius R, the measurement of absorption spectra in UV – VIS region were performed (Fig.2). The UV absorption spectra of the samples with CdS dots show that, absorption edges are shifted towards a lower wavelength (higher energy) region compared with that of bulk CdS crystal ($\square$ bulk = 494 nm corresponding to E 0 =2.51eV at room temperature). This blue shift agrees with theoretical predictions on the values of the effective bangap of
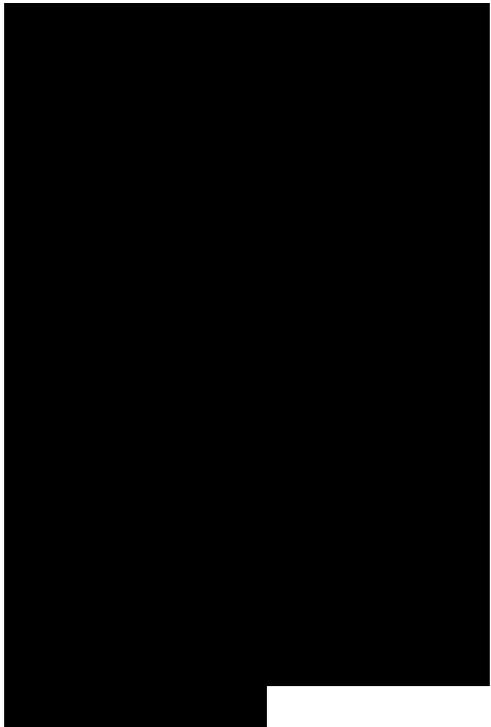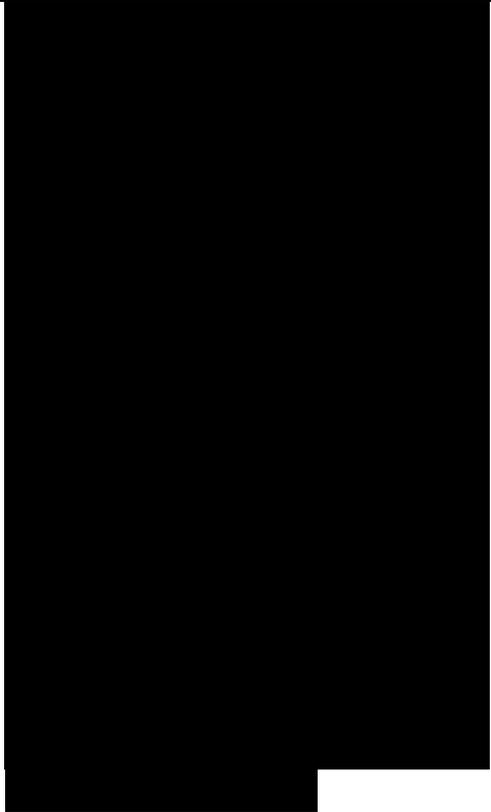
semiconductor quantum dots. A well – known formulation [11] was used to calculate the average size of CdS quantum dots through the effective bangap measure:

The blue shift was attributed to quantum effect in CdS nanocrystals.

Fig.3: Photoluminescence spectrum at 77K of the SiO2:10 % CdS sample, □exc.= 337,1 nm

Fig.4: Photoluminescence spectra at 11K of the SiO2:1 % CdS sample with excitation energy: 2.63 eV; 2.75 eV; 2.88 eV; 3.08 eV and 3.21 eV (curve 1;
2; 3; 4 and 5, respectively)

The photoluminescence's (PL) of CdS nanocrystals dispersed in SiO2 matrix exhibits the ranges, which relate to exciton levels, defect levels or shallow surface trap levels in CdS nanoparticles. Fig.3 is the typical PL spectrum of the CdS nanocrystals in the sample with 10% CdS, it was carried out under 337,1 nm line excitation at 77K. It is clearly there are tow bands in the PL. One with maximum placed at lower energy (670nm) related to defect levels or shallow surface trap levels (the origin of the surface-localized states
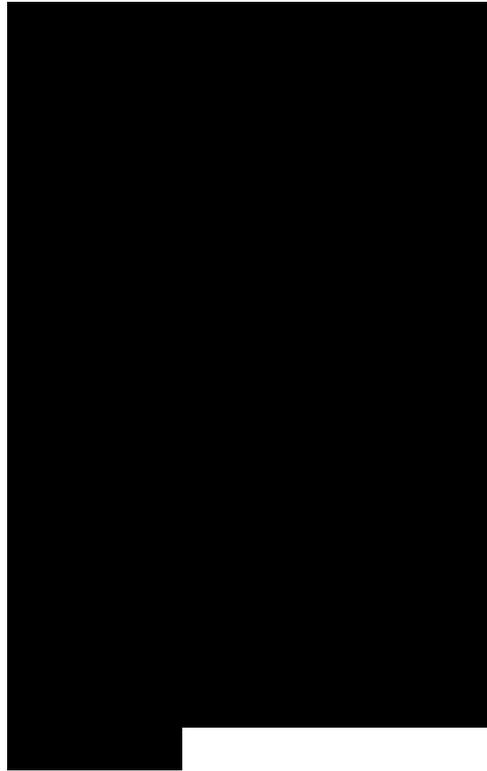
may be in Cd or S vacancies). Another centered at higher energy (456nm) is attributed to intrinsic recombination mechanism in CdS nanoparticles. Both of them are wide bands. The size distribution of nanocrystals in the sample contributes to this PL. The photoluminescence spectra at 11K of the SiO_2:1 % CdS sample in Fig.4 presents the dependence of PL on the excitation energies (or excitaion wavelengths). The curves 1; 2; 3; 4 and 5 correspond to the excitation energies 2.63 eV; 2.75 eV; 2.88 eV; 3.08 eV and 3.21 eV (respectively). The PL intensity is proportional to the amount of excited nanoparticles and to the oscillator strength of the single transitions. Under low excitation energy, only the lowest transitions of the bigger particles were excited. When the excitation energy increase, the emission of all particles in the entire size-distribution contribute to the PL.

Fig.5: The left: Photoluminescent (1) and Photoluminescent excitation spectra (2) of the sample contained 10%M CdS are recorded at 11K; the narrows indicate the positions of
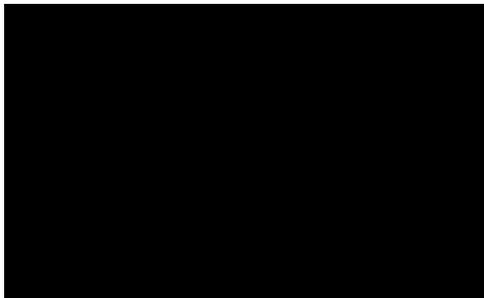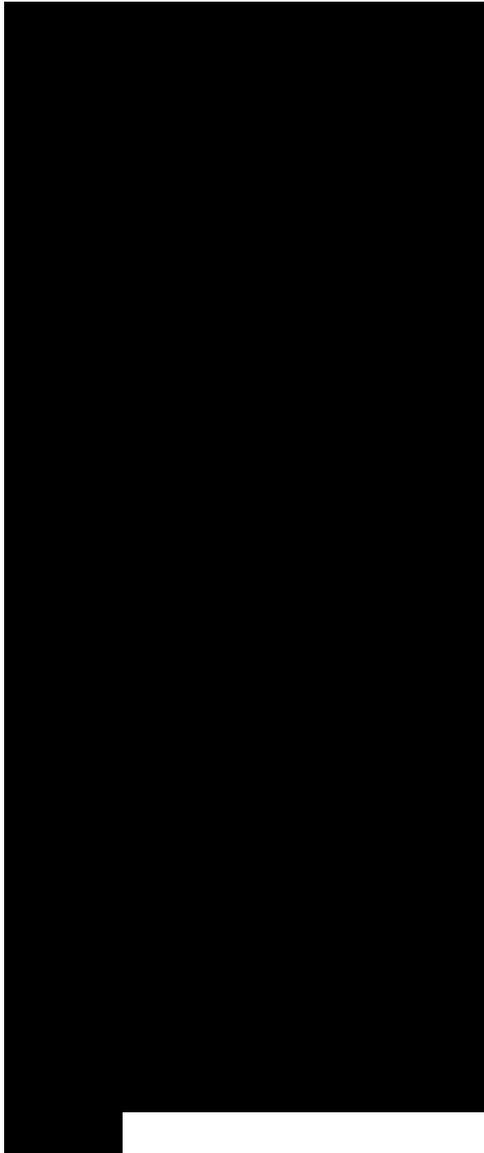
excitation (1) and detection (2) The right: scheme of the lowest energy levels observed by two experiments: PLE (a) and PL (b).

To investigate the energy levels of carries in CdS NC, the photoluminescent excitation spectra were measured. Fig.5 shows the PL spectra under 430nm excitation line of the Xenon lamp (curve 1) and the PLE with 464 nm detective wavelength (curve 2) of the sample contained 10%M CdS at 11K. The PLE reflects the informations on the relaxation mechanisms between states involved in PL. The shorter – wavelength band in the PL relates to the transitions from the exciton levels in the CdS quantum dots. These levels are governed by different terms, which constitute the Hamiltonian of electron – hole system. In the small CdS quantum dots, there are two terms of Hamiltonian wich mainly determine the size dependence of its excitonic structure: the spin – orbit interaction and the electron – hole exchange interaction. The lowest exciton level $1S3/2 – 1s$ is split by the exchange interaction into two groups wich characterized by

a total spin S = 1 for the lowest one and by S = 0 for other one (only the optical transitions from the S = 0 states to the ground state are allowed). The spin – orbit interaction spits the S = 1 states into three states characterized by a total momentum J = 2, 1 and 0 ; they are denoted A, B, and C, respectively. The S = 0 states characterized by J = 1 and is denoted D. The spin – orbit interaction mixes B and D, and states become optically allowed. In the PLE, we resonantly detected the luminescence from A (correspond to definite cluster size), the excitation via B and D give rise to two different bands as observed. In PL experiment, resonant absorption of excitation line creates allowed exciton in B. The relaxation may be by two ways: to the lowest exciton states A and through a defective level Mdef., and then to the ground state. These recombinations are observed via the two luminescence bands with P1 and P2 peaks. The differences in energy ☐E1' and ☐E2' between the detective energy and the energy of PLE maximum depend on CdS NCs size, they are correspond

to the splitting D-A and B-A, respectively. The differences in energy $\Box$E1 between the excitation energy and the energy of the shorter – wavelength band maximum in the PL also depends on CdS NCs size. It is difficult to precisely define the $\Box$E2 between the excitation energy and the energy of the longer – wavelength band maximum in the PL, because of the defective levels depend on not only CdS NCs size but on the NCs quality.

Fig.6 shows photoluminescence excitation spectra at 11K of CdS nanocrystals with various detective energies. The band maxima at 370nm in all spectrum shows the contribution to higher excited states of CdS NCs with different sizes.

Fig.6: Photoluminescence excitation spectra at 11K of the SiO2:10 % CdS sample with different detective wavelengths.

Fig.7. Photoluminescence decay for CdS NCs under 337.1 nm excitation, T= 77K.

The dynamics of PL of the samples after ultra short pulse excitation are displayed in Fig.7 (the sample of porous silica doped CdS 10 M%).
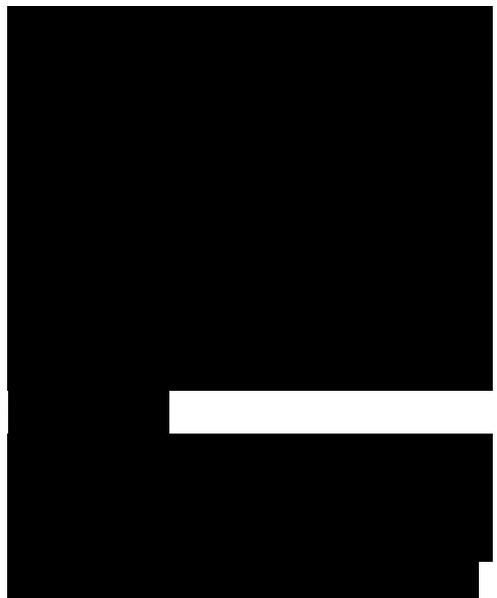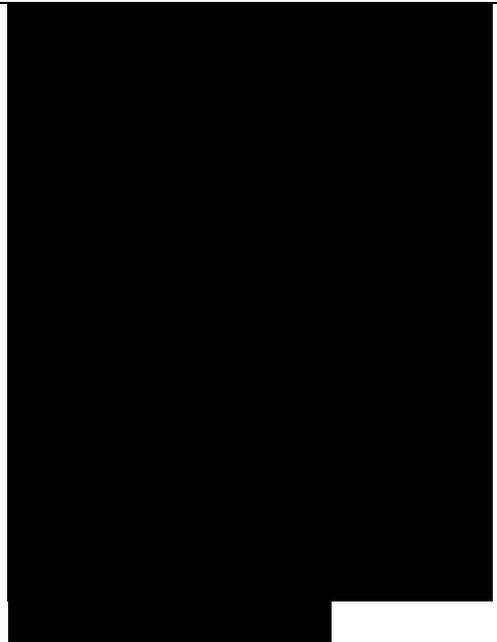
The observed luminescence decay shows a non-exponential behavior with a lifetime very short, inferior ns. The PL decays are analyzed at about the maximum of the emission band and at some different longer wavelengths in the low - energy band. The PL decay of emission line at 515 nm is faster initial decay than that of the emission line decay at 640 nm. For the time longer, they are similar; an exponential-like shape of the decay suggests it at longer times. The obtained time constant value of the faster decay τ_F is 2 ns that we believe that is the value of the radiative recombination of the interior electron - hole pair in CdS nanocrystals [9].

The luminescence from CdS nanocrystals also depends on the temperature of measurement.

Fig. 8 and Fig. 9 present the temperature dependence of the PL intensity of CdS nanocrystals dispersed in porous silica. The shape of emission band does not change, but PL intensity is dominated with the decrease of temperature. The thermal quenching of luminescence originates from the thermal ionization of electrons or
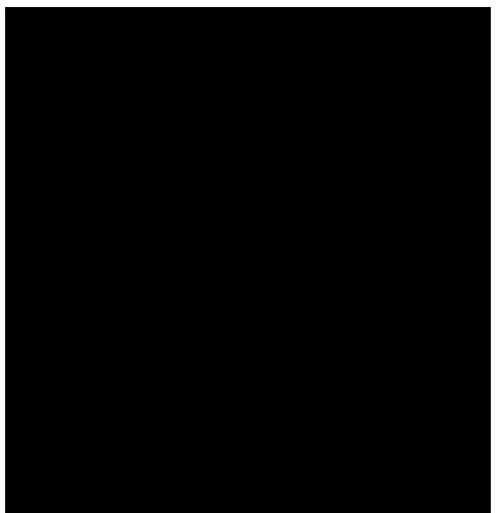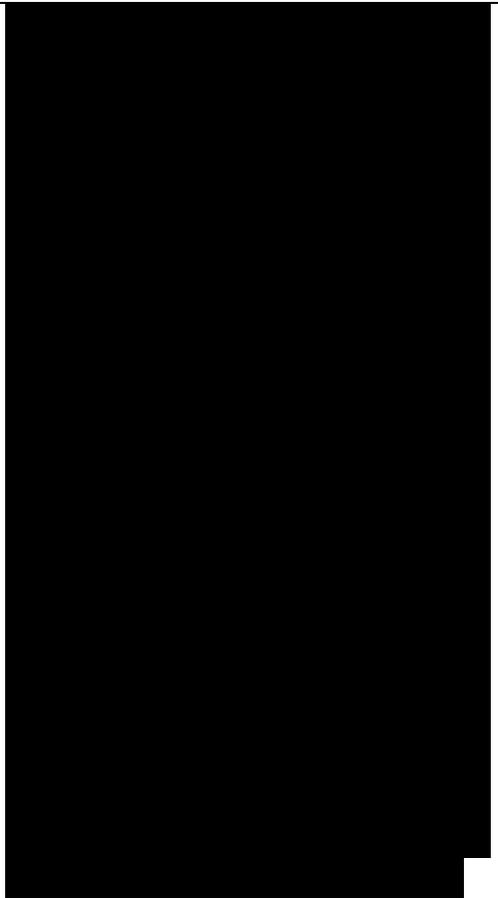
holes trapped on surface defects of CdS nanocrystals. On the other hand, the thermal activation of excitons localized at the surface of nanocrystals with surface fluctuation leads to decrease of the PL intensity [12].

Fig.8. The temperature dependence of the PL intensity of 1% CdS NCs dispersed in porous silica, λexc = 370 nm.

Fig. 9. The temperature dependence of the PL intensity of 10% CdS NCs dispersed in porous silica, λexc = 337.1 nm.

CONCLUSION

We have investigation on the luminescence of CdS (or quantum dots) dispersed in SiO2 porous matrix. The photoluminescence bands are composed of recombination of intrinsic excitons and of the defects in CdS nanoparticles. Emission features of CdS nanocrystals depend on the size of particles and excitation conditions. The bands in photoluminescence excitation (PLE) spectra show the spliting lowest exciton levels by the spin – orbit interaction and the electron – hole exchange interaction. Temperature dependence of PL intensity of CdS
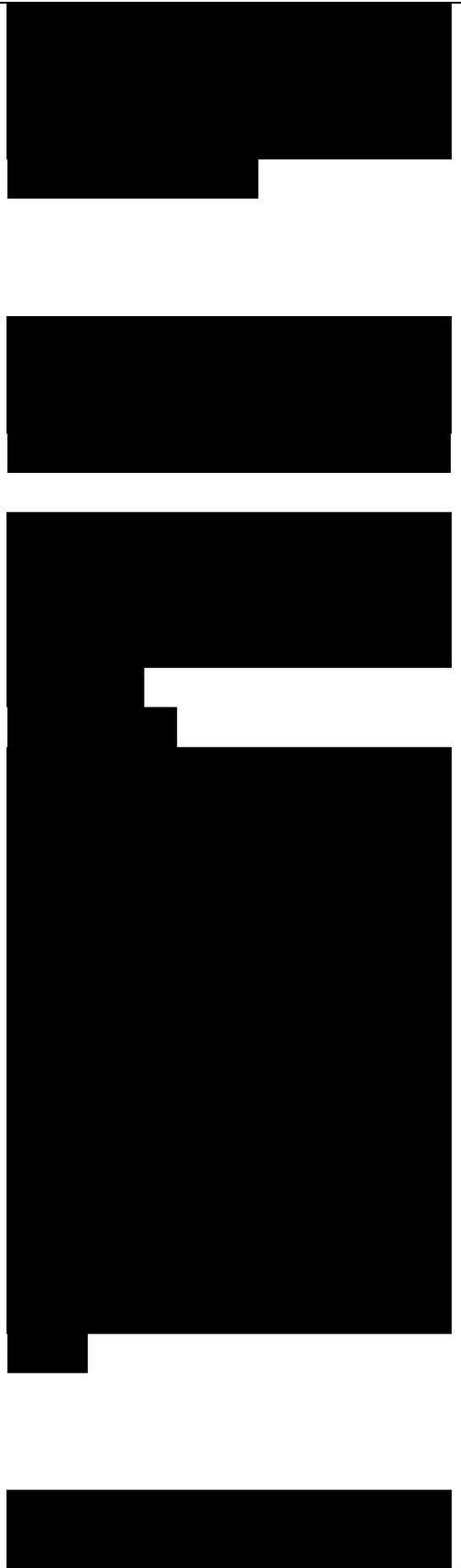
nanocrystals shows the thermal quenching of luminescence, this thermal quenching originates from the thermal ionization of electrons or holes trapped on surface defects of CdS nanocrystals and the thermal activation of excitons localized at the surface of nanocrystals. The lifetime of CdS NCs is very short which inferior nanoseconds.

Experimental spectra show the presence of the quantum confinement effect into small CdS dots.