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M. V. Artemyev

SEMICONDUCTOR NANOCRYSTALS INSIDE SPHERICAL MICROCAVITIES: A CASE OF QUANTUM DOTS IN PHOTONIC DOTS

This paper describes the latest experiments with semiconductor nanocrystals combined with various types of microspheres. Since the discovery of size quantization effect in chemically synthesized semiconductor nanocrystals they transformed to a very popular and useful object for studying the optical properties of zero-dimensional semiconductor nanostructures (quantum dots, QD). Sharp excitonic resonances in absorption spectra of CdSe, CdTe, CdS and other semiconductor nanocrystals reflect the existence of discrete energy levels inside such dots which allowed one day to call them «artificial atoms». Additionally, II–VI nanocrystals prepared via special high temperature reaction in coordinating solvents exhibit high photoluminescence quantum yield above 20 % at room temperature. That immediately brought the nanocrystals into the experiments on single dot spectroscopy [1]. Due to intrinsic size distribution of semiconductor nanocrystals their absorption, as well as photoluminescence spectra are inhomogeneously broadened. Within common 5–7 % size deviation the low temperature photoluminescence linewidth of QDs ensemble is about 20-40 meV, while single dot spectroscopy revealed the homogeneous linewidth of single QDs dropped down to 60–100 μeV below 20 K. Usually, the more complex core-shell (CdSe)ZnS nanocrystals are ulitized in the optical experiments, since epitaxially grown 1–2 monolayers of ZnS shell on CdSe core give drastic increase in PL quantum yield (up to 70–80 % at room temperature) and photostability [2]. Incorporation of QDs having ultranarrow emission bands inside high-quality optical microcavity allows to study the interaction between quantized electron states of QDs and discrete photon states of microcavity [3].

The concept of low-dimensional semiconductor nanostructure with discrete electron levels incorporated inside optical microcavity was realized earlier with quantum wells placed between two Bragg mirrors (Distributed Bragg Reflector, DBR) both grown by molecular beam epitaxy. Later, epitaxially grown QDs have been utilized in the same configuration [3]. While, epitaxial QDs represent rather pseudo-zero-dimensional island-like structures, chemically synthesized *true zero-dimensional* spherical QDs can not be incorporated into DBR structure and other methods should be involved. Recently, there were few attempts to incorporate CdSe nanocrystals into polymeric micron-size spheres which represent simplest fully three-dimensional spherical microcavities [4, 5]. Due to large mismatch between refractive indices of polymer (1.5–1.6) and air (1.0) the light emitted by QDs inside microspheres undergoes total internal reflection at the polymer-air interface and is forced to circulate inside

microsphere. For certain wavelength of light there exists constructive interference and allowed photon mode appears. Otherwise, destructive interference brings about forbidden photon modes for other wavelength [6]. As the result, a number of discrete lines instead of single broad band appears in the PL spectrum of QDs in single isolated microsphere. These photon modes are called often Whispering Gallery Modes (WGM). The similarity between quantization of electron states in QDs and photon states in microspheres has provoked to name them as *photonic dots*. The linewidth of photon modes is determined by quality factor $Q = \omega/2\gamma$ and is a parameter of microsphere diameter, surface flatness, shape perfection. It is assumed also, that the material of microsphere does not absorb appreciably in the spectral region of QDs emission. Taking into account that PL bands of CdSe QDs lie in the visible region the row of materials for preparation of high quality microspheres is limited by glass, quartz and few polymers, like polystyrene (PS) and polymethylmethacrylate (PMMA).

Our earlier experiments we began with PMMA microspheres randomly doped with core-shell (CdSe)ZnS QDs [4]. PMMA as a material for microspheres has been chosen since it does not show appreciable intrinsic luminescence (contrary to PS) when excited by blue and near-UV lasers. The microspheres were prepared by emulsion polymerization of methylmethacrylate to which QDs were added prior to emulsification. The resulting solid PMMA microspheres of 5-20 mm in diameter were placed onto quartz support and examined by micro-PL optical equipment. In Fig. 1 both room temperature PL spectra of QDs, and PMMA@QDs are presented.

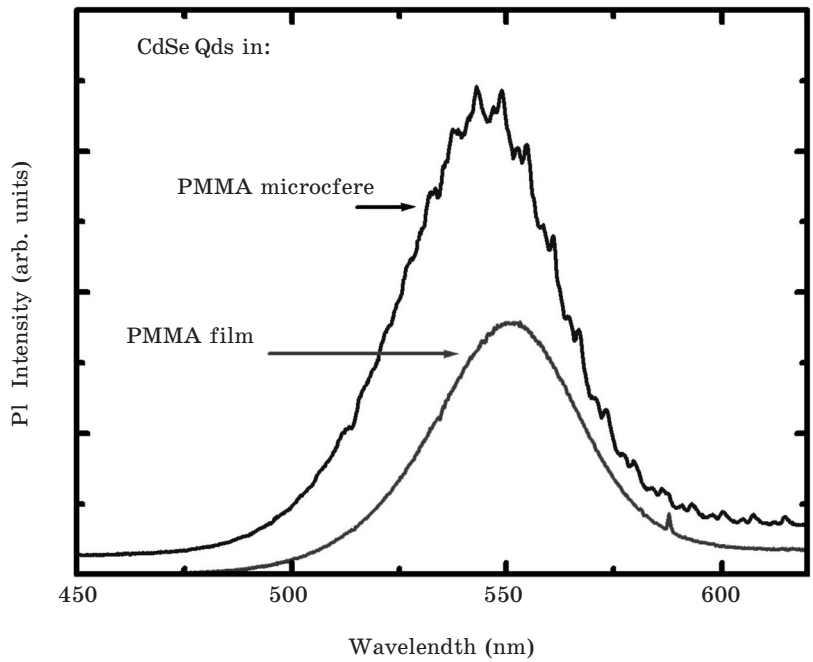

Fig. 1. Room temperature micro-PL spectra of (CdSe)ZnS QDs incorporated in planar PMMA film and single 10 μm in diameter PMMA microsphere. The excitation source is He-Cd laser (λ = 354 nm, P = 5 mW)

While, (CdSe)ZnS QDs alone have shown nearly Gaussian PL band centered at 2.25 eV the PL spectrum of single 10 mm in diameter PMMA microsphere doped with QDs exhibited a periodic fine structure superimposed on Gaussian band. The periodicity of fine structure was more pronounced in differential PL spectrum obtained by subtracting overall Gaussian background from experimental PL spectrum. This fine periodic structure arises from light emitted by QDs and coupled to WGM's. It should be pointed out that magnitude of fine structure on first PMMA@CdSe microspheres was not exceeded 10 % of total PL band intensity and most part of PL band remained unmodulated. Only a small fraction of quantum of dots inside PMMA microsphere was coupled to WGM's, while the rest of them gave a background PL signal. The theory of WGM's shows that the light can be coupled most efficiently to modes with quantum number $n = 1$ and a radial distribution of electromagnetic field for this mode is maximum nearly the surface of microsphere[6]. Since, our first microspheres were doped by QDs nearly randomly over full their volume, naturally, most dots located deep away of near-surface region and have brought a large unmodulated PL signal. Additionally, the Lorentz fit of the linewidth of cavity modes resulted in $2\hbar\lambda = 0{,}004$ eV and corresponding quality factor of 500, which is too small to observe interesting phenomena related to cavity quantum electrodynamics. These two negative moments compelled us to search for other *quantum dots in a photonic dot* structures with higher Q-factor and effective dot-WGM coupling.

In the nex step we have developed the method for preparation of hollow polymeric microspheres with air core and PMMA shell doped with (CdSe)ZnS QDs [7]. The core-shell photonic dot with empty core allows to remove unmodulated PL background due to presence of QDs only in a shell where the emission is effectively coupled to WGM's. The preparation of hollow PMMA microsphere is based

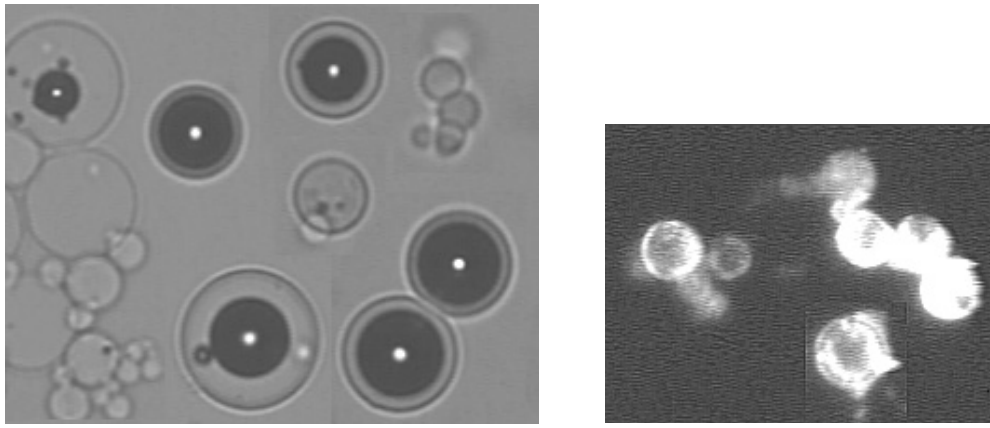

Fig. 2. (left) Optical microscopy image of hollow PMMA microspheres doped with (CdSe)ZnS QDs. Microspheres are in immersion liquid (glycerol). (right) Room temperature PL image of hollow PMMA@QDs microspheres. The excitation source is Ar-ion laser (λ =488 nm). The average diameter of microspheres is 7 μm

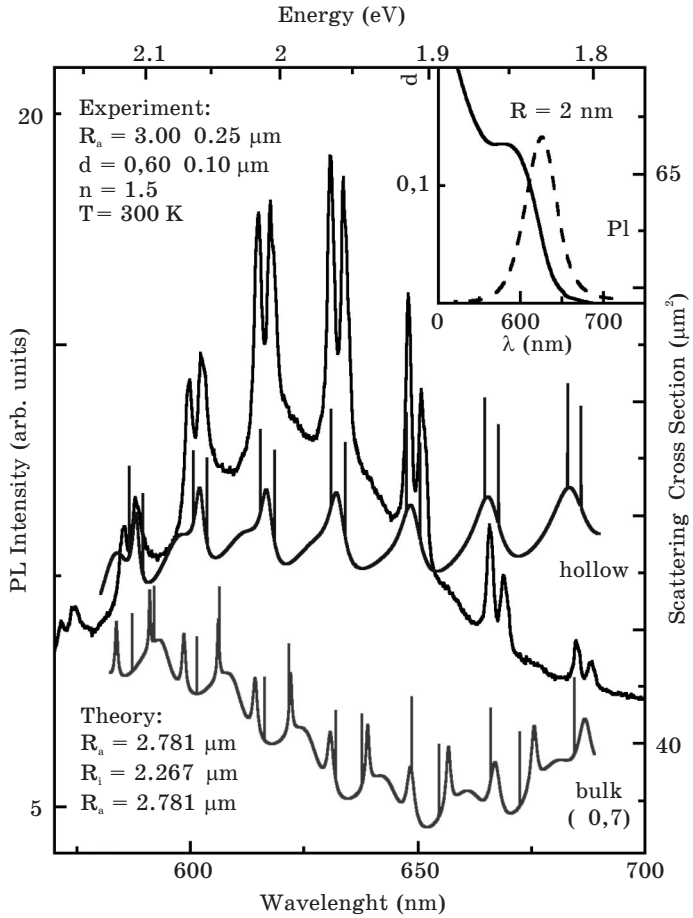

Fig. 3. Room temperature PL spectrum of single hollow PMMA@QDs microsphere (upper curve) and calculated WGM structure for corresponding hollow (middle) and bulk (lower) PMMA microspheres of the same radius. The excitation source for PL spectrum is Ar-ion laser (λ = 488 nm)

on idea of using a water microemulsion of PMMA and QDs dissolved in volatile solvent methylmethacrylate (MMA). PMMA and QDs are readily dissolved in MMA which in turn is not miscible with water. In order to create a microemulsion a prolonged sonication of water-MMA mixture was done with hexadecyltrimethylammonium bromide (HTAB) as a surfactant. A room temperature slow evaporation of MMA from microemulsion brings the formation of a suspension of solid PMMA microspheres in water. PMMA microspheres preserve a spherical form of initial MMA microdroplets. Surprisingly, evaporated MMA leaves solid PMMA shell instead of that to form a solid kernel. PMMA shell is growing in the direction from surface to the center of initial MMA droplet. After complete evaporation of MMA the hollow (air-filled) core left with solid PMMA shell in which all dissolved QDs are displaced. Fig. 2 shows an optical microscopic image of hollow

PMMA microspheres together with PL images. The utilization of immersion liquid allows to visualize clearly the existence of hollow core due to mismatch between refractive indeces of PMMA/glycerol ($n \approx 1{,}55$) and air core ($n = 1$). In Fig. 3 the PL spectrum is shown for single hollow PMMA microsphere doped with (CdSe)ZnS QDs. The Q-factor of such microsphere is within the range of 2000–4000 for n = 1 mode. The quality of hollow microspheres could be further improved by adjusting the preparation conditions. Due to absence of QDs at the center of hollow microsphere the residual PL background in Fig. 3 can be attributed to the coupling of light to the modes with higher n. The profiles of n = 1 and n = 2 WGMs have been calculated and experimental modes assigned very well.

To further increase the Q-factor we searched for other types of microspheres made of materials different from PMMA. The most serious problem with quality of self-made PMMA microspheres arised from their some non-sphericity and rough polymeric surface. Likewise, in case of hollow microspheres there is an additional problem related to non-homogeneity of PMMA shell thickness. The roughness of PMMA microsphere surface results in a strong damping of WGMs due to light scattering. We stopped on commercial 5–10 micron in diameter glass microspheres. These microspheres usually are prepared by flame melting of glass powder with subsequent fast cooling. During the melting of glass grain in a gas-flow regime a microdroplet of liquid glass takes a spherical shape and extremely flat surface due to surface tension forces. The fast cooling of glass microdroplets in a gas flow brings about nearly atomic surface flatness of solid microspheres. Because, (CdSe)ZnS QDs can not survive through the high-temperature procedure of glass powder melting (>500 ^{o}C) we developed the method for chemical attachment of QDs to the surface of ready glass microspheres. This method is based on well-known self-assembling approach. Briefly, glass microspheres were treated first with mercaptopropyltrimethoxysilane (MPTS) which bounds to the glass surface via Si-O-Si bonds. The remaining mercapto groups –SH are directed away from the glass surface. Then, surface modified microspheres were treated with colloidal solution of QDs in appropriate solvent. The QDs are attached to the surface of microspheres via S-Zn bonds between MPTS mercapto groups and surface zinc atoms of QDs. Finally, the structure represents a glass microsphere covered with surface submonolayer of chemically attached QDs. The «submonolayer» means, that attached QDs do not create a close-packed 2D layer. QDs are separated rather by a distance of few d (diameter of QD).

Fig. 4 demonstrates room temperature emission spectra of ensemble of (CdSe)ZnS QDs attached to single isolated glass microsphere and plain glass, as a reference object. QDs without spherical microcavity shows a Gaussian band centered at nearly 2 eV with FWHM about 150 meV. It is well-established such broad band arises from certain size distribution of QDs in ensemble. For comparison, room temperature emission spectrum of single QD is shown with linewidth only about twice less, than of large QDs ensemble. The low temperature drastically decreases the linewidth of single QD. We have obtained readily the value of 90 meV which is consistent with data from other groups [1]. Fig. 4 also demonstrates the photon mode structure of single 3,1 μm in radius glass microsphere with QDs on the surface. The single mode linewidth has been determined precisely to be less than 300 meV by using high-resolution spectrometer and calculated Q-factor was close to 10^4. Therefore, glass microspheres and (CdSe)ZnS QDs at their surface allow to achieve two

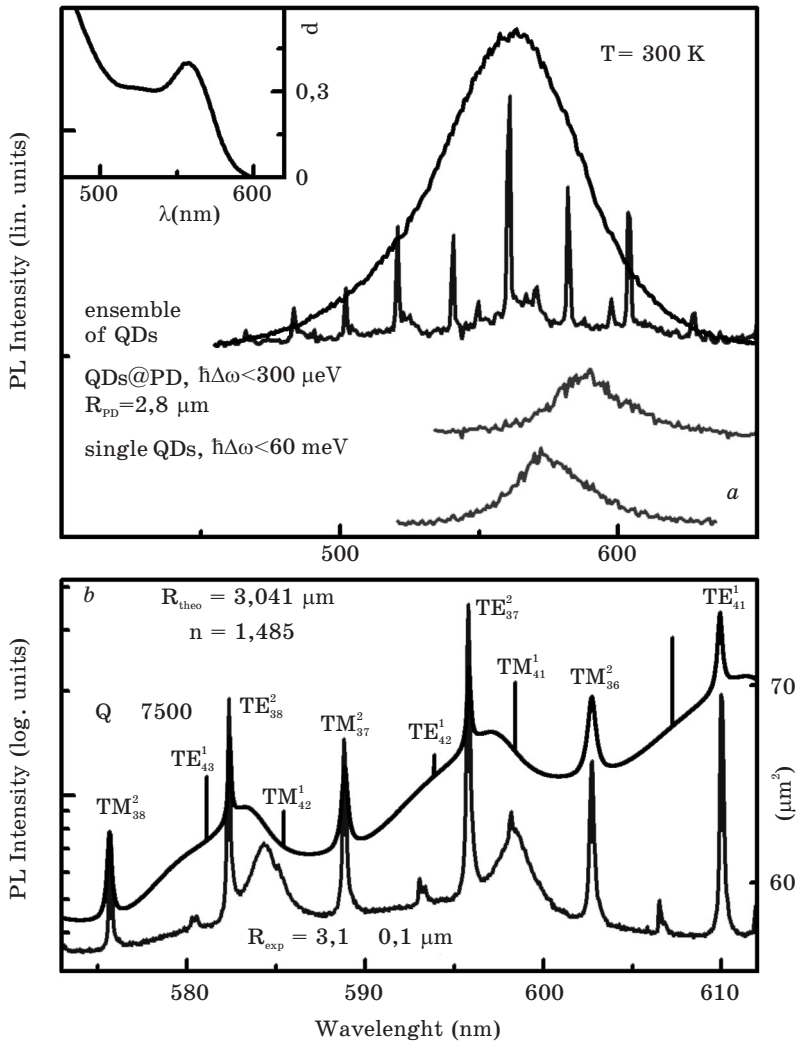

Fig. 4. a) Room temperature emission spectra of ensemble of (CdSe)ZnS QDs, single glass microsphere (R = 3.1 mm) covered with QDs and single Qds on plain quartz. Inset: Absorption spectrum of ensemble of Qds. The excitation source is Ar-ion laser (λ = 488 nm), pump intensity is 50 W/cm^2. Emission is detected by microscope objective with N/A=0.95, an imaging spectrometer and CCD camera.
b) High resolution emission spectrum of the same microsphere around 595 nm and calculated scattering cross section of R = 3.1 μm glass microsphere with mode assignment

different regimes by varying the temperature: when the linewidth of single QD is larger (room temperature), or close to the linewidth of photon mode (cryogenic temperature). This two different regimes bring to different optical phenomena in a spherical microcavity. Fig. 5 illustrates the situation, when the room temperature

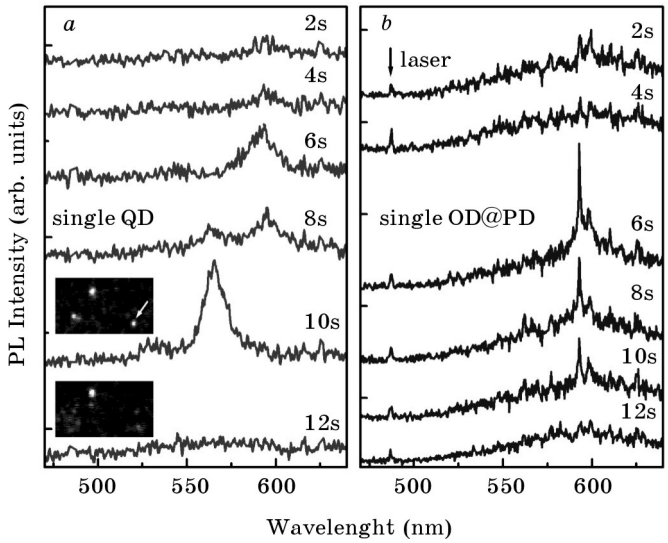

Fig. 5. a) Room temperature sequence of a single QD PL spectra without microcavity demonstrating an effect of blinking and spectral jumps. *b*) Room temperature sequence of single QD@PD demonstrating the coupling of QD emission to PD modes. The excitation source is Ar-ion laser (λ = 488 nm). Emission is detected by microscope objective with N/A = 0.95, an imaging spectrometer and CCD camera

emission from single QD is coupled to single photonic dot mode. It is well-established now that chemically synthesized QDs, like our (CdSe)ZnS nanocrystals exhibit PL blinking and spectral jumps in single-dot time-domain spectra. The blinking in microsecond through seconds range arises from temporal trapping of photoexcited carriers on deep and shallow defect levels, mostly related to QD surface dangling bonds. The trapped electron or hole switches QD into «dark» state: any subsequent photogenerated electron-hole pair must recombine nonradiatively via Auger mechanism involving previously trapped carrier which results in an «off» state. Simultaneously, trapped carriers distort and shift the electron levels of QD resulting in spectral jumps of emission. It is important in our case, that spectral jumps in single (CdSe)ZnS QD emission ($\approx$ 100 meV) are within the range of photon mode spacing. During spectral jumps the single QD PL band time-by-time meets neighboring photon mode and couples to it. The most important consequence of this process is that *single photon mode is controlling the linewidth of single QD emission!* A certain increase in a number of QDs per single photonic dot brings to the situation, when each photon mode is occupied only by few QDs and we observe a phenomenon of *photon mode blinking*. Hense, spherical microcavity works as a collector for broad band QD emission concentrating them into few ultranarrow photon modes which, in turn is favorable condition to achieve a room temperature lasing in single photonic dot doped with Qds.

For studying the room temperature lasing in *quantum dots in a photonic dot* structures we used pulsed excitation by optical-parametric oscillator pumped by Nd-YAG laser. The low-repetition rate pulsed beam (30 Hz) allowed to avoid the strong heating of sample and thermal destruction of QDs. Fig. 6 shows the intensity-dependent PL spectra of single 5 μm in diameter glass microsphere covered with submonolayer of (CdSe)ZnS QDs. The important result here is that not all photon modes exhibit a threshold-like behavior with increased pump power being of generally accepted indication of lasing. The mode at 618 nm shows definitely intensity-dependent line narrowing and threshold behavior, while two left and right neighboring modes have rather linear response versus intensity (the left mode also saturates at highest intensities). That is, a mode competition takes place at early stage of lasing development. A plot of mode intensity versus pump power exhibits slope close to 1 in double-log scale which is a hint on non-biexcitonic mechanism of lasing in our experiment. Yet, these results may be evaluated as precursor for room temperature lasing in spherical microcavities doped with QDs and sufficient improvement of optical quality of microspheres and emitting properties of QDs has to be achieved. The drastic increase in the concentration of QDs per single PD also is a way to get lasing. There is no possibility to put much more QDs on the surface of glass microsphere and polymeric microspheres seem to be good candidates. QDs can be impregnated in sufficient quantity into subsurface

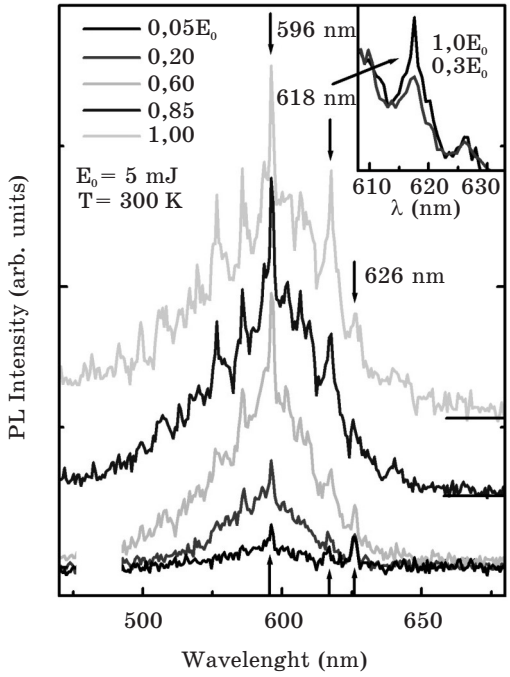

Fig. 6. Room temperature emission spectra of QDs@PD at different pump intensities of pulsed excitation with 3ns (λ = 490 nm) pulses from optical-parametric oscillator pumped by Nd-YAG laser (30 Hz).

regions of polymeric microspheres via widely used methods for polymeric fluorescent beads.

Low-temperature experiments with QDs@PD structures allows to get a very interesting information about the dynamics of radiative emission of 3D-confined electron states coupled to discrete photon states in a spherical 3D microcavity. A cavity quantum electrodynamics predicts the enhancement of spontaneous emission rate inside high-Q microcavity. In 1946 Purcell was first, who theoretically has shown that for radio frequency range [8]. For our QDs@PD structures we should expect an enhancement of spontaneous emission rate when $\Delta\omega_{QD} \le \Delta\omega_{caw}$ i.e. the lifetime of photons inside microcavity is shorter than the radiative lifetime of QDs in a vacuum. We have found that for 5 mm microsphere at 20K the single QD emission linewidth approaches corresponding mode linewidth and above mentioned condition is fulfilled ($\Delta\omega_{QD} \sim 300$ μeV, $\Delta\omega_{caw} \sim 285$ μeV). The Purcell factor F determines the modification of spontaneous emission rate $F = \tau_{free}/\tau_{cav} = 2Q(\lambda_c/n)^3 (4\pi^3 V_{eff})$, where the important parameters are quality factor Q and mode volume V_{eff}. The best Q achieved in 5 μm glass microspheres reaches ~10^4 and rises further with increasing diameter, while the effective volume also increases with microsphere size. Therefore, there exists an optimal diameter of microsphere (around 3.5–5 μm) in order to attain a maximum F.

We started our time-resolved experiment from comparison of PL decay time for various QD structures, like CdSe nanocrystals in glass matrix, colloidal CdSe and (CdSe)ZnS core-shell QDs. CdSe dots in glass normally show a nearly monoexponential PL decay at low temperature [9]. In contrary, CdSe dots synthesized by high-temperature colloidal chemistry possess a non-monoexponential decay perhaps, due to prevailing recombination through surface traps. The growth of ZnS shell on CdSe core removes most of defects and PL decay curve approaches monoexponential form accompanied with drastically increased PL quantum yield. We registered PL decay curves using picosecond Streak camera and 120 fs frequency-doubled Ti:sapphire laser as excitation source. The two samples have been prepared, one containing 5 μm glass microspheres and another (reference) with small pieces of glass from broken microspheres, both covered with the same surface submonolayer of (CdSe)ZnS QDs [10]. This approach guarantees the identity of all chemical parts (QDs, glass, surface chemical modification) in both samples. The difference between samples arises only from coupling of QDs emission to microcavity WGMs in first sample and a free space in the second one.

Fig. 7*a* shows low temperature PL spectra of single 5 mm glass microsphere with QDs and QDs on glass without microcavity. The calculated Q-factor of this microsphere is nearly 9000. In order to avoid any misinterpretations we have registered PL decay curves for both samples at the same wavelength indicated by arrow in figure. This wavelength corresponds to sharp mode at 586,7 nm. The normalized decay curves are plotted in Fig. 7 (*b*-*c*). The logarithmic scale allows to demonstrate a nearly monoexponential character of curves at early time followed with extended long-time tail. For the different cavity modes the decay rates in a cavity are enhanced by a factor of up to 5. We also compared the decay times in on- and off-resonance to cavity modes and found, that in off-resonance the decay time is likely decreased and characterized with very small enhancement factor. The off-resonant emission comes rather from PL background of QDs inefficiently

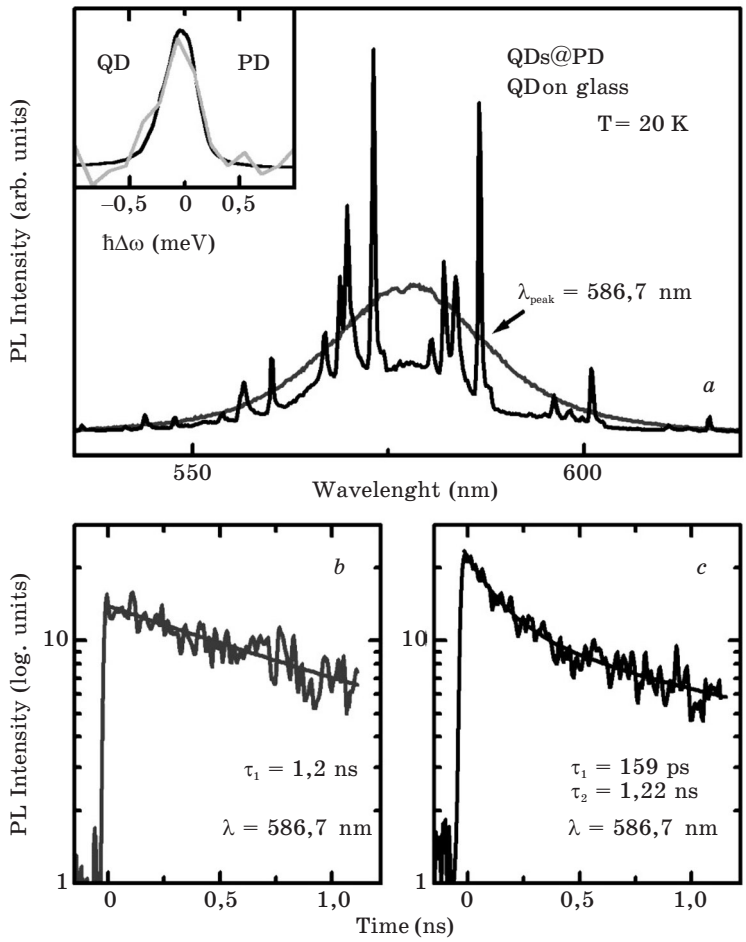

Fig. 7. *a*) Low temperature emission spectra of Qds with and without microcavity. Inset. High resolution low temperature single QD emission band linewidth in comparison with PD mode. *b*) Low temperature PL decay (in semi-log scale) of QDs without microcavity. *c*) Low temperature PL decay (in semi-log scale) of QDs in microcavity. The data were obtained with picosecond streak camera (20 ps resolution), the excitation source is 120 fs, 445 nm frequency-doubled Ti-sapphire laser

coupled to microsphere WGMs. Therefore, the highest enhancement factor relates to high-Q modes where the light propagates within a small ring close to the surface with very small mode volume. We estimated a Purcell factor for such a ring with cross-sectional area of the order of $(\lambda_c/n)^2$ and $F \sim 2–10$ depending on the quality factor Q. This estimated value is within the data obtained in our experiment.

Using the micro-PL optical setup with polarization-selective detection and imaging spectrometer we have developed the mode-mapping method for spherical micro-

cavities doped with QDs [11]. Most of CdSe QDs absorb and emit polarized light[1] especially those of highly elongated or rod-like shape [12]. The polarization control of both position and orientation of QDs in spherical microcavity, as well as the selective excitation of either transverse electric (TE) or magnetic (TM) modes would be highly relevant. We mapped the spatially and spectrally resolved intensity of QDs@PD emission on and off resonance to cavity modes for fixed polarization plane. If fix the polarizer orientation parallel to *z* axis the TE modes will appear as bright regions in the equatorial plane of emission intensity map. The TM modes will have the maximum intensity perpendicular to TE modes and form bright spots at the poles. For the experiment we selected rather small microsphere of 1.8 μm in radius because the TE and TM mode assignment for such small microsphere can be done using Mie theory (for larger microspheres the numerical efforts increase drastically with size). Then, we compared the results of mode mapping with calculated mode polarization in order to proof our concept. The calculated mode structure fairly well agrees with experimental PL spectrum. As we expected in an emission maps the intensity decreases at the poles for TE modes and at the equatorial plane for TM modes. Therefore, the developed polarization-sensitive detection scheme can be utilized to the more complex mode spectra of much larger microspheres, where the direct calculations of mode structure may fail.

In colclusions, the polymeric or glass microspheres containing (CdSe)ZnS nanocrystals represent a new class of *quantum dots in a photonic dot* structures. We observed experimentally a number of interesting optical effects including single QD and single mode blinking, precursor for room temperature lasing, cavity induced enhanced spontaneous emission rate (Purcell effect). When seriously improve the optical quality of microspheres, as well as emission properties of quantum dots we expect to achieve the condition for realization of other interesting cavity quantum electrodynamics effects like vacuum Rabi splitting in single QD@PD structure.

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REFERENCES

1. Photoluminescence from single semiconductor nanostructures / S.A. Empedocles, R. Neuhauser, K.Shimizu e.a. // Adv. Mater. 1999. Vol. 11. P. 1243–1256.
2. Highly luminescent monodisperse CdSe and CdSe/ZnS nanocrystals synthesized in hexadecylamine-trioctylphosphine oxide mixture / D.V. Talapin, A.L. Rogach, A. Kornowski e.a. // Nano Letters. 2001. Vol. 1. P. 207–211.
3. *Yamamoto Y., Tassone F., Cao H.* Semiconductor Cavity Quantum Electrodynamics. Heidelberg: Springer-Verlag, Berlin, 2000. 154 p.

4. *Artemyev M., Woggon U.* Quantum dots in photonic dots // Appl. Phys. Lett. 2000. Vol. 76. P. 1353-1355.
5. Coupled semiconductor nanocrystals to a fused-silica microsphere: a quantum dot microcavity with extremely high Q factor / X. Fan, P. Palingidis, S. Lacey e.a.// Opt. Lett. 2000. Vol. 25. P. 1600–1602.
6. *Chang R.K., Chamillo A.* (Eds.). Optical Processes in Microcavities. Adv. Series in Appl. Phys. Vol. 3. World Scientific, Singapore, 1996.
7. *Artemyev M., Woggon U., Wannemacher R.* Photons confined in hollow microspheres// Appl. Phys. Lett. 2001, Vol. 78. P.1032–1034.
8. *Purcell E.* Phys. Rev. 1946. Vol. 69. P. 681.
9. *Woggon U.* Optical Properties of Semiconductor Quantum Dots. Springer Tracts in Modern Physics 136. Heidelberg: Springer-Verlag, Berlin, 1997.
10. Light trapped in a photonic dot: Microspheres act as a cavity for quantum dot emission / M. Artemyev, U. Woggon, R. Wannemacher e.a.// Nano Letters. 2001. Vol. 1. P. 309–314.
11. Mode identification in spherical microcavities doped with qunatum dots/ B. Moller, M. Artemyev, U. Woggon e.a.//Appl. Phys. Lett. 2002. Vol. 80. P. 3253-3255.
12. Linearly polarized emission from colloidal semiconductor quantum rods/ J. Hu, L.-s. Li, W. Yang e.a. // Science. 2001. Vol. 292. P. 2060-2063.