The luminescence properties of colloidal quantum dots

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Abstract. Luminescent properties of systems containing lead sulfide (PbS) nanoparticles deposited on substrates of porous silicon (p-Si), oxidized porous silicon (OPS) and have been studied. It was shown that structure of the matrix and its composition are of crucial importance affecting luminescence spectra of colloidal quantum dots by setting their radiation wavelength.

1. Introduction
For the last decade colloidal quantum dots (CQDs) have become an object of particularly intensive studying. CQDs are semiconductor particles of nanometer scale synthesized in liquid media and characterized by unique properties which substantially differ from bulk material properties. Important advantages of CQDs are simplicity of size tunability through technological parameters variation (time, temperature etc.) and that synthesis procedures do not require expensive equipment and materials. Placing the quantum dots in porous matrixes lead to additional advantages due to stabilization of their size and increasing density of emitting centers. Such structures are promising materials for a high-performance light-emitting diode (LED) and laser structures, as well as photosensitizers in solar cells or luminophores in micro-devices for optical tomography of biological tissues.

2. Materials and methods
In present report we investigate luminescence of lead sulfide (PbS) CQDs synthesized via pyrolysis of metalorganic compounds with organic systems containing a source of sulfur [1-6]. As a result of synthesis CQDs with various sizes were obtained. After measurements of photoluminescence spectra of CQDs in an solution QDs CQDs were deposited on various silicon substrates [7-9]. Monocrystalline silicon (mono c-Si), purified porous silicon (por-Si) and porous silicon oxidized in air for 14 days were employed as substrates [10-12]. Porous silicon was obtained by anodic electrochemical etching in a one-compartment cell in electrolyte based on hydrofluoric acid supplemented with isopropyl alcohol. Size of the pores ranged from 10 to 40 nm.

In order to investigate properties of CQDs, methods of non-invasive optical spectroscopy were applied. The photoluminescence spectra was investigated with a laboratory setup based on a double monochromator spectrometer SDL-1 [13,14]. A Nd:YVO4 diode-pumped solid-state laser with doubled frequency (λ = 532 nm) and a semiconductor laser diode with the emission wavelength of λ = 445 nm were used as sources of exciting radiation.

3. Results
In a first phase, we studied luminescent properties of PbS CQD samples in the solution. The PbS CQD photoluminescence spectra are shown in Figure 1. For further investigation we chose two types of samples with a maximum of their spectral response at 950 nm (PbS-1) and 1000 nm (PbS-2) Preliminary theory-based estimate of CQD size gave values of 4-5 nm. Besides, we observed a
significant spectral broadening (the half-width exceeded 100 nm) indicating a considerable spread of particle sizes. Altering of particle sizes was carried out via variation of process parameters of CQD synthesis such as temperature and time.

![Figure 1. PL spectra of PbS CQDs in the solution](image1)

We also studied luminescent properties of porous silicon substrates. In contrast to bulk silicon crystals such materials shows a significant emissivity because of photon emission from nanorods and nanowalls [6], and can partially be caused by surface states. PL spectra of studied samples are shown in Figure 2. The maximum of spectral response was at the wavelength of 660 nm. The spectrum half-width was about 150 nm due to the spread of particle sizes and other parameters of nanosystems in the substrate.

![Figure 2. The luminescence spectra of the oxidized substrate with deposited quantum dots and without.](image2)

Porous substrates were found to significantly influence PL spectra of PbS CQDs, while the use of mono-Si blank substrates did not result in major changes of luminescent properties of the nanoparticles. When particle settling onto the porous substrates was carried out immediately after anodic treatment, modification of PL spectrum was relatively small (Figure 3). However significant
shift of the maximum to shorter wavelengths was reached with porous silicon substrates oxidized in air during 14 days.

![PL spectra of PbS CQD deposited on the porous substrate or in solution](image)

**Figure 3.** PL spectra of PbS CQD deposited on the porous substrate or in solution

The initial colloidal solution contains QDs of various sizes. In case of unoxidized substrate, pore diameter could be oversized to considerably affect the size of particles entering into the pores. When using the substrate based on oxidized porous Si, the pore size reduces due to oxide formation. As a result smaller nanoparticles enter into the pores, that is selection takes place. When the nanoparticles are being applied and distributed over the substrate surface, decomposition of larger particles takes place which followed by selection of newly formed smaller particles. These phenomena result in decreasing the sizes of the emitting particles, and, consequently, in increasing the energy of the emitted photons.

The presence of particle selection is confirmed by the fact that initial size of the particles practically had no effect on the emission spectrum of the particles precipitated into the oxidized matrixes (Figure 4).

![PL spectra of PbS CQD deposited on the substrate.](image)

**Figure 4.** PL spectra of PbS CQD deposited on the substrate.
We also found that deposition PbS CQDs onto surface of porous Si results in alteration of substrate PL spectra. PL spectra of porous Si samples without nanoparticles and structures of oxidized por-Si are shown in Figure 2. When depositing of QD they are distributed in pores and in immediate vicinity from the nanosystems inside the porous matrixes. It changes wave functions of the Si nanostructures and their energy level positions resulting in splitting or broadening of the levels. And with this, the effective band gap energy reduces, and the PL peak shifts into longer wavelengths which is similar to interaction of coupled quantum wells. When the barrier is very thin, this system transforms into a quantum well where the width is twice as much as the initial well, and the levels of the new well are lower. We estimated the width of such a QW and level positions and demonstrated a satisfactory fit between the simulation and experimental results.

4. Discussion and conclusion
Thus, it has been found out that interactions between quantum dimensional elements of the porous Si-PbS QDs nanosystem result in a shift of por-Si PL spectra and a change in the photoluminescent properties of PbS QDs. We established that PbS CQDs produced by chemical deposition onto por-Si matrixes have a luminescence in the infrared spectrum region but with the spectrum maximum shifted to shorter wavelengths. It was shown that matrix structure and its composition are of crucial importance affecting luminescence spectra of CQDs by setting their radiation wavelength.

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6. References
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