

Optical properties of InP/ZnS quantum dots deposited into nanoporous anodic alumina

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Abstract. Spectral characteristics of InP/ZnS core/shell colloidal quantum dots of two different sizes (QD-1 and QD-2) were investigated. Absorption and luminescence spectra were analyzed for a series of solutions with a concentration range from 0.04 to 40 g/l. Energies of the optical transitions are evaluated. The obtained values of 2.60 eV (QD-1) and 2.38 eV (QD-2) correspond to the InP first excitonic transitions while 4.06 (QD-2) and 4.70 eV (QD-1, QD-2) are assumed to be caused by the ZnS shell absorption. Structures based on nanoporous anodic aluminum oxide (AAO) with the QDs were synthesized via an electrochemical oxidation and ultrasonic-assisted deposition. Chromaticity coordinates and correlated color temperatures for all phosphors under study were calculated. The fabrication possibilities of InP/ZnS@AAO nanostructures with tunable emission color (including the border of white region) were shown.

1. Introduction

Colloidal quantum dots (QDs) attract much attention and research efforts over the past decades [1,2,3]. Generally, a size of this semiconductor nanocrystals should be comparable with the exciton Bohr radius or the electron and hole de Broglie wavelength of the material they are made of. Such condition leads to the manifestation of the quantum-confinement and therefore to a collapse of the continuous energy bands of a bulk material into discrete, atomic-like energy levels [4]. Moreover, the electronic structure strongly depends on the dot size providing these objects with tunable physical and chemical properties. At present, possible applications of QDs in many fields are intensively studied, in particular for creating light-emitting diodes, lasers, solar cells, phosphors, biosensors and biomarkers, etc [5-9].

QDs based on III-V semiconductor compounds are of special interest, because they do not contain toxic components such as Cd, Pb and Hg, which have low acceptability for technological applications. Indium phosphide is the most studied compound, as the emission of InP nanocrystals can be tuned throughout the visible and near infrared range by changing their size [10]. Their overgrowth with wider band gap ZnS shell is used to improve rather poor optical properties of as-prepared InP nanocrystals [10]. However, synthesis of the InP-based QDs emitting in the blue region with a high quantum yield (QY) is the challenging task. In this regard, the use of widegap solids is promising to create luminescent composites with adjustable emission based on discrete color mixing. Nanoporous anodic alumina characterized by a large surface area and intrinsic blue emission [11] can be used as functional substrates for constructing such phosphors. Thus, this work deals with optical and luminescence study of the InP/ZnS colloidal QDs deposited into anodic aluminum oxide (AAO) matrices.



2. Experimental

InP/ZnS colloidal QDs of two different sizes marked DS-72a (QD-1) and DS-72b (QD-2) were synthesized by FSUE "NIIPA" (Dubna, Russia). They have core/shell structure coated with modified polyacrylic acid. Semiconductor nanocrystals are dispersed in water with initial concentrations (c) of 40 g/l for QD-1 and 48.4 g/l for QD-2. OA measurements of the samples were carried out at room temperature in a range of 190 to 900 nm by means of a Shimadzu UV-2450 spectrophotometer in a 1 cm quartz cuvette. A slit width and sampling interval were set to the 2 and 0.1 nm, respectively. Absorption spectra of the QDs were recorded for a series of solutions with a concentration range from 40 g/l to 0.04 g/l prepared by two-fold dilutions with distilled water for 10 times. Photoluminescence (PL) of the QDs was analyzed for the colloidal solutions by means of a Perkin Elmer LS 55 luminescent spectrometer in a fluorescence mode at room temperature.

QYs of the semiconductor nanocrystals under investigation were determined relative to the standard according to the procedure reported in [12]. Rhodamine 6G (R6G) was chosen as a reference since it is considered as one of the well-established standards [13] and its emission region is close to that of the QDs. First of all water solutions with absorbance $A \approx 0.5$ at a 370 nm wavelength were prepared. Afterward they were diluted in a volumetric ratio of 1:9 in order to avoid inner filter effects [14]. Finally, their fluorescence spectra were detected, areas under emission curves calculated and QYs evaluated.

Nanoporous matrices of Al_2O_3 were grown by two-step Al foil anodizing at the constant current density using oxalic acid as an electrolyte [10]. The synthesized AAO structures with the average pore size of ≈ 80 nm were annealed at 500 and 700 °C for 5 hours in ambient atmosphere. All the samples had amorphous structure in accordance with the X-ray diffraction analysis [10]. To deposit QDs the AAO substrates were placed in the InP/ZnS colloidal solutions and treated in an Eurosonic 4D ultrasonic bath for 60 minutes. Four structures were obtained this way. Their PL measurements under 270 nm excitation in a range of 300 to 700 nm were performed in a fluorescence mode at room temperature using LS55. A sampling interval, excitation and emission slit widths were 0.5, 10 and 5 nm, respectively.

3. Results and discussion

3.1. Optical absorption and photoluminescence of InP/ZnS quantum dots

Electronic energy structure of semiconductor nanocrystals appears in the OA spectra. They are presented in figure 1 for colloidal QD-1 and QD-2 solutions of various concentrations. It can be seen that the QDs begin to absorb light in different spectral ranges. Namely, QD-1 has an $A = 0.1$ at a wavelength of 560 nm and the QD-2 – at a wavelength of 600 nm for $c=40$ g/l. When diluting different regions of the spectrum are spanned by absorbance range of $A = 0.1 - 3$, which allows absorption of samples to be studied in a wide diapason of wavelengths revealing its features. The QD-1 OA exhibits a distinct peak in the region of 450-480 nm after several dilutions. For QD-2 a shoulder in the range of 490-570 nm is observed. This fact can be connected with the wider particle size distribution for the second type colloidal nanocrystals or with different quantum confinement regimes in the samples. Experimental OA spectra are also influenced by light scattering at nanocrystals, which should be taken into account when evaluating optical transition energies. In addition, the concentration dependencies were analyzed at various wavelength. Observed linear character indicates the absence of deviations from the Beer–Lambert–Bouguer law for $c = 0.04 - 40$ g/l.

A known method for distinguishing of the hidden peaks is derivative spectrophotometry [3,15]. For the all experimental data $d^2A/d\lambda^2$ spectra were calculated. For instance, figure 2 shows some OA curves and their second derivatives whose minima correspond to the hidden absorption maxima. The technique was used to evaluate energies of the optical transitions. Obtained values are 2.60, 4.70 ± 0.02 eV for the QD-1 and 2.38, 4.06, 4.68 ± 0.02 eV for the QD-2 and do not depend on the solution concentration. The energies of 2.60 and 2.38 eV correspond to the first excitonic absorption peaks of the InP core and the shift between them results from size-dependent effect. Noteworthy that the values

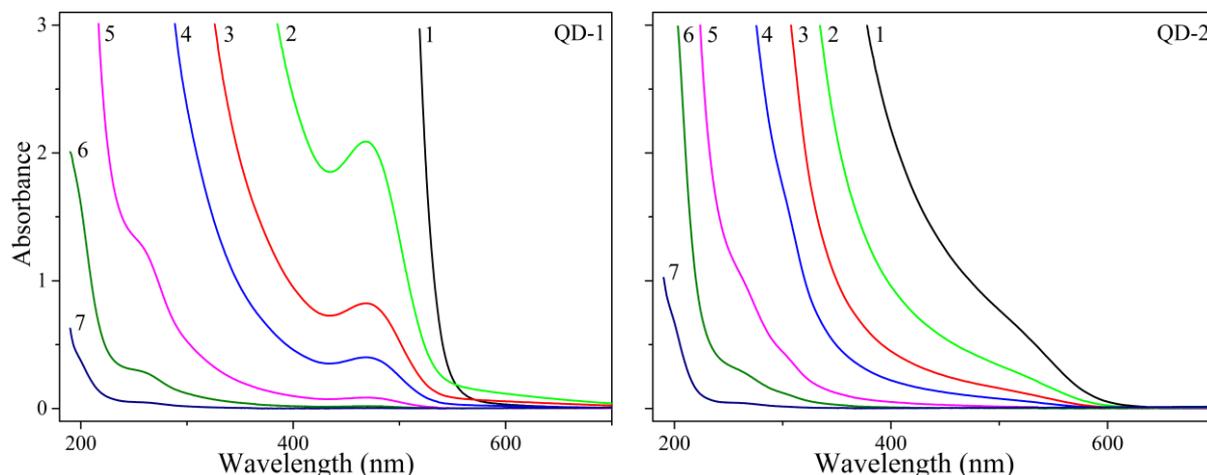


Figure 1. OA spectra of the InP/ZnS solutions of various concentrations.
QD-1: 1 – 40 g/l, 2 – 10 g/l, 3 – 5 g/l, 4 – 2.5 g/l, 5 – 0.63 g/l, 6 – 0.16 g/l, 7 – 0.04 g/l;
QD-2: 1 – 40 g/l, 2 – 20 g/l, 3 – 10 g/l, 4 – 5 g/l, 5 – 2.5 g/l, 6 – 0.31 g/l, 7 – 0.04 g/l.

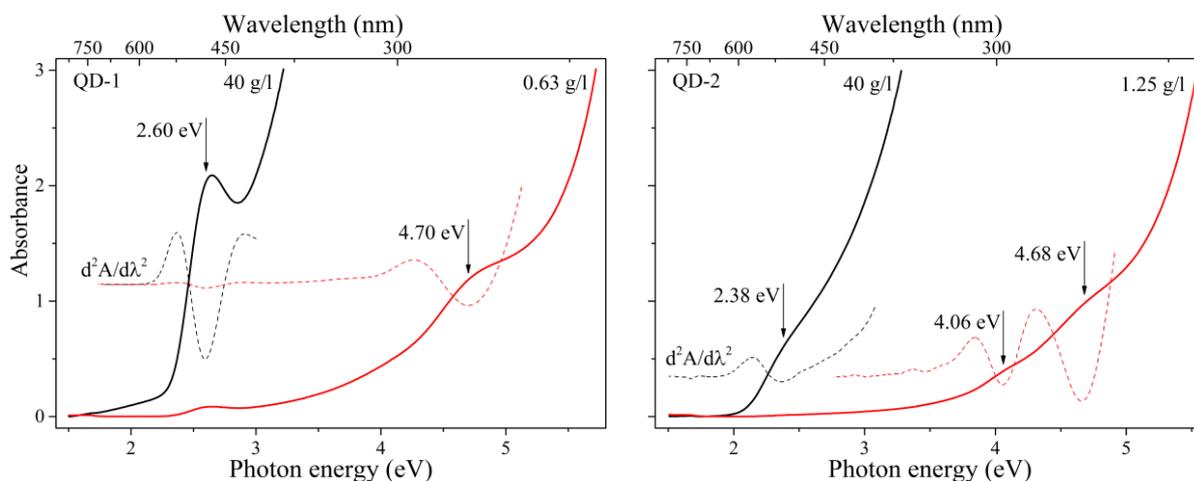


Figure 2. OA spectra for QDs of the marked concentrations (solid lines) and their second derivatives (dash lines). The arrows indicate minima of the $d^2A/d\lambda^2$ curves.

of 4.68 and 4.70 eV are equal within the experimental error and fall in the range of band gap energies from 4.82 eV to 4.47 eV observed for nanocrystalline zinc sulfide powders [16]. In [17] the absorption edge of the ZnS colloidal nanocrystals is determined to be 4.07 eV, which matches with our data for the QD-2 samples. Thereby these optical transitions might be ascribed to the ZnS shell, however clarifying their origin requires additional researches.

PL measurements were carried out for the InP/ZnS solutions of the same concentration range as for OA. The QD-1 has $h\nu_{\max} = 2.38$ eV (525 nm), FWHM = 0.25 eV and QD-2 exhibits $h\nu_{\max} = 2.18$ eV (570 nm), FWHM = 0.33 eV (green and orange dash lines in figure 3). The analysis of the data registered indicates that emission maxima is not affected by the concentration. QYs under excitation of 370 nm are 27% for the QD-1 and 10% for the QD-2 solutions.

3.2. Photoluminescence of InP/ZnS@AAO nanostructures

PL spectra under the 270 nm excitation of the synthesized structures based on AAO membranes with the deposited QDs are demonstrated in figure 3. Cyan and blue dash lines display the emission of aluminum oxide matrices annealed at 500 and 700 °C. Black solid lines illustrate PL of the corresponding fabricated structure. The spectra of the synthesized phosphors contain luminescence bands of the QD-1 and QS-2. This result agrees with our previous work [8] where another type of InP/ZnS semiconductor nanocrystals ($h\nu_{\max} = 2.26$ eV, FWHM = 0.23 eV) was deposited into AAO matrices. Preservation of the fluorescence emission properties of the QDs after the deposition suggests a reliable passivation of the its surface.

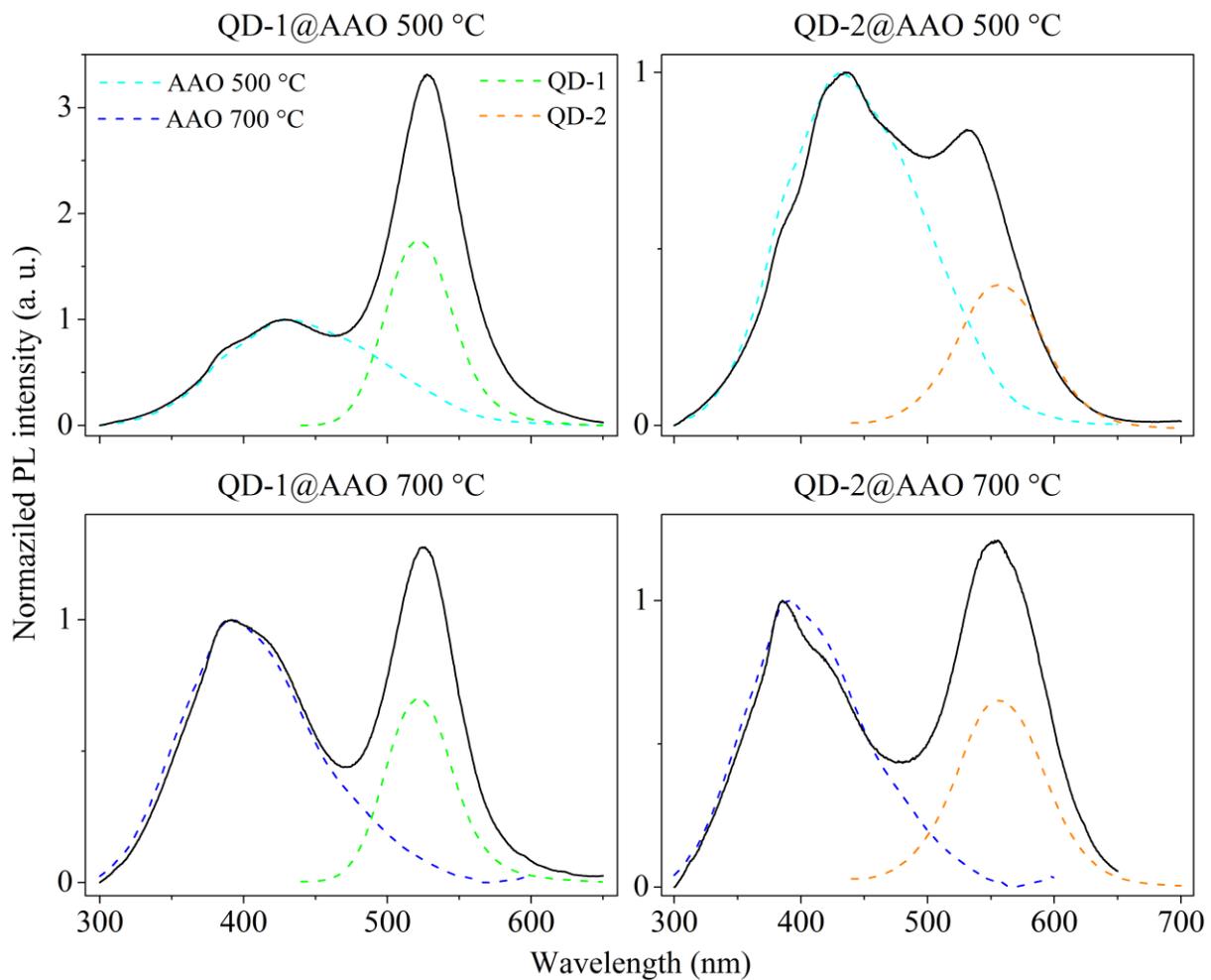


Figure 3. PL spectra of synthesized InP/ZnS@AAO structures.

Figure 4 shows chromaticity diagram where appropriate calculated coordinates for the samples under study are marked and photos of the fabricated phosphors are presented. Circles indicate objects synthesized here and triangles refer to the [8]. It is seen that phosphors with the tunable emission color can be designed by filling AAO membranes with InP/ZnS QDs of various sizes. AAO matrices annealed at 500 and 700 °C with deposited QD-2 (6 and 8 diagram points) exhibit luminescence on the border of the white region. Correlated color temperatures for these phosphors are 4068 K and 3232 K, respectively. Obtained data for all samples are summarized in table 1.

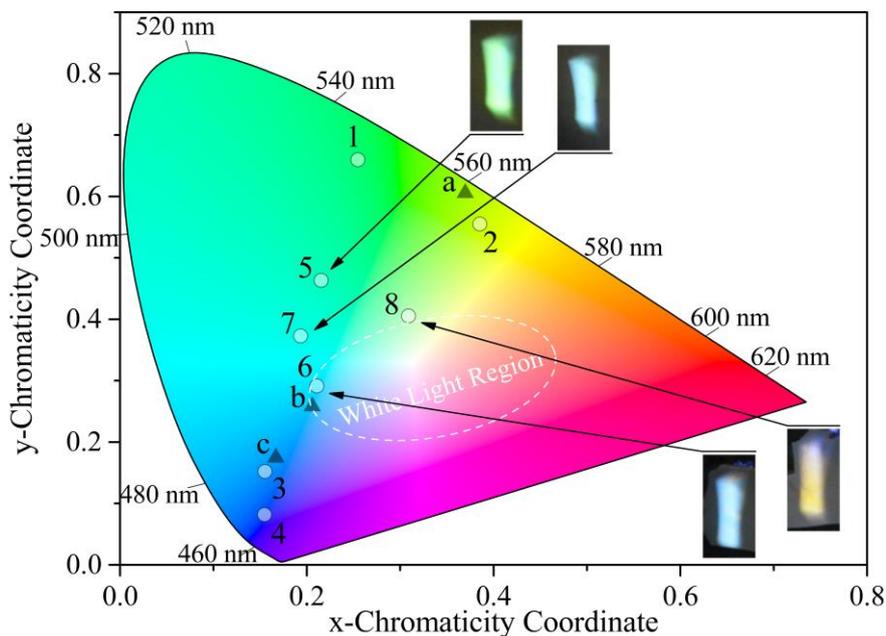


Figure 4. Chromaticity diagram for the samples.

Table 1. Calculated chromaticity coordinates.

Diagram point	Sample	Coordinates
1	QD-1	(0.25, 0.66)
2	QD-2	(0.39, 0.56)
3	AAO 500 °C	(0.16, 0.15)
4	AAO 700 °C	(0.15, 0.08)
5	QD-1@ AAO 500 °C	(0.22, 0.46)
6	QD-2@ AAO 500 °C	(0.21, 0.29)
7	QD-1@ AAO 700 °C	(0.19, 0.37)
8	QD-2@ AAO 700 °C	(0.31, 0.41)
a	InP/ZnS [8]	(0.37, 0.61)
b	InP/ZnS @ AAO 500 °C [8]	(0.21, 0.26)
c	InP/ZnS @ AAO 700 °C [8]	(0.17, 0.17)

4. Conclusion

InP/ZnS core/shell colloidal QDs of two different sizes were investigated. OA and PL spectra were studied for a series of the QD-1 ($h\nu_{\max} = 2.38$ eV) and QD-2 ($h\nu_{\max} = 2.18$ eV) solutions within a concentration range from 0.04 to 40 g/l. The OA experimental data were analyzed by techniques of derivative spectrophotometry characterize hidden absorptions features. Energies of the optical transitions are evaluated to be 2.60, 4.70 ± 0.02 eV for the QD-1 and 2.38, 4.06, 4.68 ± 0.02 eV for the QD-2. The values of 2.60 eV and 2.38 eV correspond to the InP excitonic absorption peaks. Other transition are assumed to be caused by the ZnS shell. The calculated values as well as measured maxima of the QD emission bands do not depend on the solution concentration. Quantum yields of the samples evaluated relative to the R6G aqueous solution are 27% for the QD-1 and 10% for the QD-2.

Phosphors based on nanoporous aluminum oxide membranes with core/shell InP/ZnS semiconductor nanocrystals were synthesized via an anodizing process and ultrasonic-assisted deposition. The fabricated InP/ZnS@AAO samples with QD-2 exhibit emission on the border of the

white region. The nanostructures are characterized by chromaticity coordinates of (0.21, 0.29), (0.31, 0.41) and correlated color temperatures of 4068 K, 3232 K.

Acknowledgments

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