

An Experimental Setup for Analysis of Weak Photoluminescence in the Near-Infrared Spectral Region^{1, 2}

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Abstract—In this paper, we describe the experimental setup for analysis of spectral and kinetic photoluminescence parameters in near-infrared spectral region. The setup allows to carry out photoluminescence (PL) measurements in a spectral range of 900–1700 nm, temporal range of 1 ns–100 μs, and temperature range of 77–400 K. The performance of the setup is demonstrated with PL spectra and decay curves obtained for lead sulfide quantum dots monolayer and highly diluted lead sulfide quantum dots solution.

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INTRODUCTION

Last decade showed the increasing research interest to the near infrared (NIR) spectral region (700–2000 nm). NIR-emitting materials are widely used in telecommunications and optoelectronics. A lot of materials are nowadays known to possess luminescence in this spectral region, such as organic dyes, lead halide perovskites [1], porous silicon [2], semiconductor quantum dots [3, 4], carbon dots [5], singlet oxygen and the materials doped with rare-earths. Photoluminescence (PL) analysis is the most common method for investigation of energy level structure, charge carrier dynamics and relaxation processes in such materials. A fast growth in the NIR materials synthesis and applications requires the high-sensitive and tunable experimental equipment which allows both spectral and kinetic PL analysis.

EXPERIMENTAL, RESULTS

In this paper, we present an experimental setup for the NIR photoluminescence measurements capable of working with colloidal and thin-film samples. The setup scheme is shown in Fig. 1. The grating monochromator Acton 2150i with 300 mm⁻¹ grating (blaze $\lambda = 1.2 \mu\text{m}$) provides linear dispersion of 19.5 nm/mm. Highly sensitive InGaAs/InP avalanche photodiode (APD) “MicroPhotonDevices” operating in photon counting mode is used for light detection. The use of photon counting mode allows us to perform both steady-state and time-resolved measurements without

the need to change the detector. The spectral range of the APD sensitivity covers the wavelengths from 900 to 1700 nm.

To achieve efficient PL excitation for a wide range of the studied objects, it is crucial to have a set of pumping sources. Instead of using a broad-spectrum lamp with its own monochromator or a parametric laser, we apply a set of different laser excitation sources. To achieve an easy switch between sources, optical fibers are used to drive the excitation radiation to the sample. This solution suffers from slight reduction of the excitation light power due to the losses comes from the coupling light into fiber. At the same time, the use of lower excitation intensity is preferable due to the possible photodegradation of the samples.

PL signal is collected utilizing a 90° scheme. Pumping light from the excitation source is coupled to the optical fiber and forms a parallel beam outside the optical fiber’s exit collimator. The resulting beam is focused on a sample with a lens with a focal length of 50 mm. The PL is collected with a converging lens with a focal length of 50 mm and focused onto the monochromator entrance slit. The light passed through the monochromator is focused to the fiber-coupled collimator, which is connected to the detector. Photodiode control unit is connected to Acton SpectraHub interface module, used for further signal processing. A spectral sensitivity curve shown in Fig. 2 was obtained using a black body source with colour temperature of 978 K. The best performance of the detector depends on the experimental parameters (excitation type, PL signal power, etc.) and can be adjusted using the previously adopted settings [6].

To perform the analysis of temperature dependencies of PL parameters, the experimental setup is

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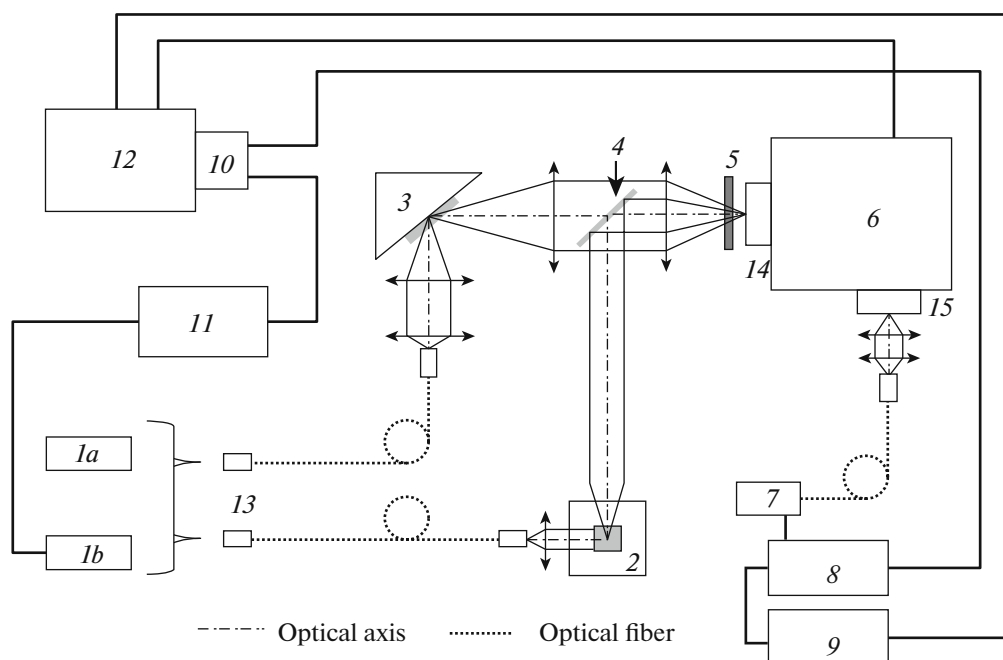


Fig. 1. The scheme of the experimental setup. *1a*—CW-excitation light sources; *1b*—pulsed laser sources; 2—cuvette holder; 3—3D-positioner for thin films/thermostat cell; 4—flip gold mirror; 5—pumping light filter; 6—diffraction monochromator; 7—InGaAs/InP avalanche photodiode; 8—APD control unit; 9—“SpectraHub” interface module; 10—photon correlator; 11—external generator; 12—PC; 13—collimators; 14—monochromator entrance slit; 15—monochromator exit slit.

equipped with a liquid-nitrogen thermostatic cell Linkam THMS-600. The cell operates with a Linkam LNP94/2 flow control unit and a Linkam TMS94 control unit. The use of the cell enables the measurements in the temperature range from 77 to 400 K.

Using the described setup, we were able to measure PL from PbS quantum dots (QDs) colloidal solution with a concentration of 5×10^{-8} M and from PbS QDs thin film with a thickness of 1–2 monolayer. Resulting PL spectra with a spectral resolution of 9 nm are

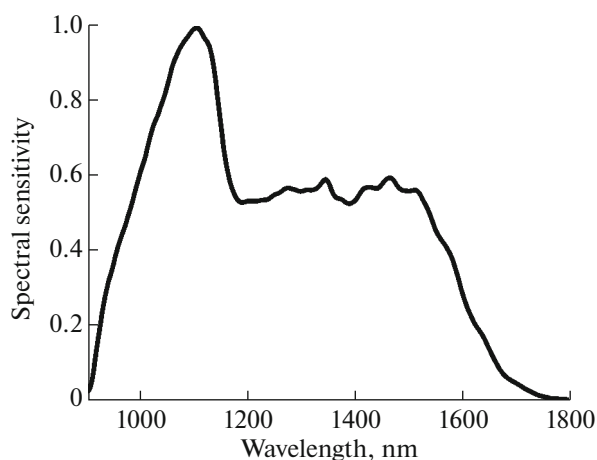


Fig. 2. Spectral sensitivity of InGaAs/InP avalanche photodiode (MicroPhotonDevices).

shown in Fig. 3. A cw-LED ThorLabs M530F2 ($\lambda = 530$ nm, output power measured at the fiber exit is 6 mW) is used as an excitation light source. Assuming the Gaussian shape of the PL spectra we can fit it to improve the results of the measurements. Acceptable signal-to noise ratio can be obtained with relatively small acquisition time: from 10 to 20 minutes.

For the time-resolved mode measurements, a number of pulsed lasers with different wavelengths, repetition rates, pulse energies and pulse widths, can be used:

—PicoQuant PDL 800-B with laser heads LDH-P-C-635B ($\lambda = 635$ nm, pulse energy 0.4 nJ, pulse width <90 ps) and LDH-P-C-980B ($\lambda = 980$ nm, pulse energy 0.15 nJ, pulse width <90 ps). Repetition rate can be adjusted up to 20 MHz.

—Laser-Export DTL-339QT with different wavelengths $\lambda = 351, 527, 1053$ nm, pulse width <10 ns, pulse energy varying from 7 to 36 μ J for repetition rate 5 and 1 kHz, respectively.

—Standa STA-01SH-1, $\lambda = 532$ nm, pulse width <1 ns, pulse energy 5 μ J, repetition rate up to 5 kHz.

Variety of available pulsed laser excitation sources allows the registration of PL decay from the samples with different PL lifetimes. Thus, the PL decay time constants as small as a few nanoseconds can be obtained. To operate in time-resolved mode, APD is connected to PC-integrated DPC-230 photon correlator (Becker & Hickl GmbH). Time-resolved operation modes, performance and special aspects for used

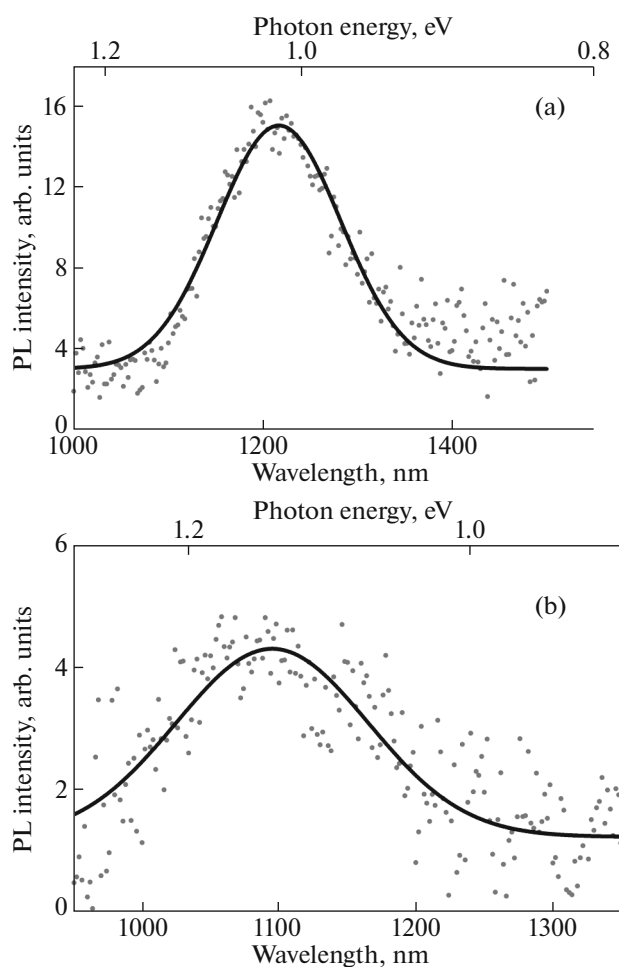


Fig. 3. PL spectra for 4.3 nm PbS quantum dots in (a) tetrachloromethane, concentration 5×10^{-8} M; (b) Langmuir–Blodgett thin film (1–2 QD layers).

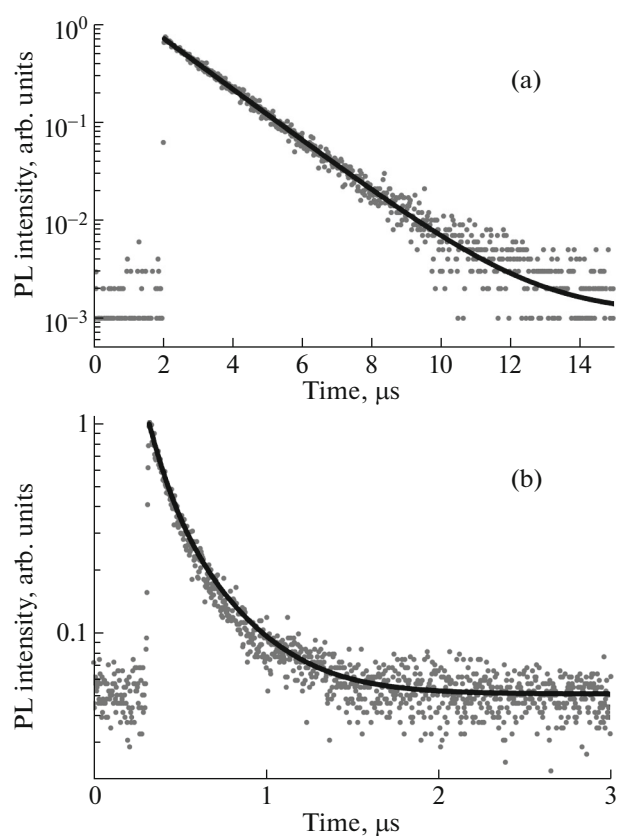


Fig. 4. PL decay curves for 4.3 nm PbS quantum dots in (a) tetrachloromethane, concentration 5×10^{-8} M; (b) Langmuir–Blodgett thin film (1–2 QD layers).

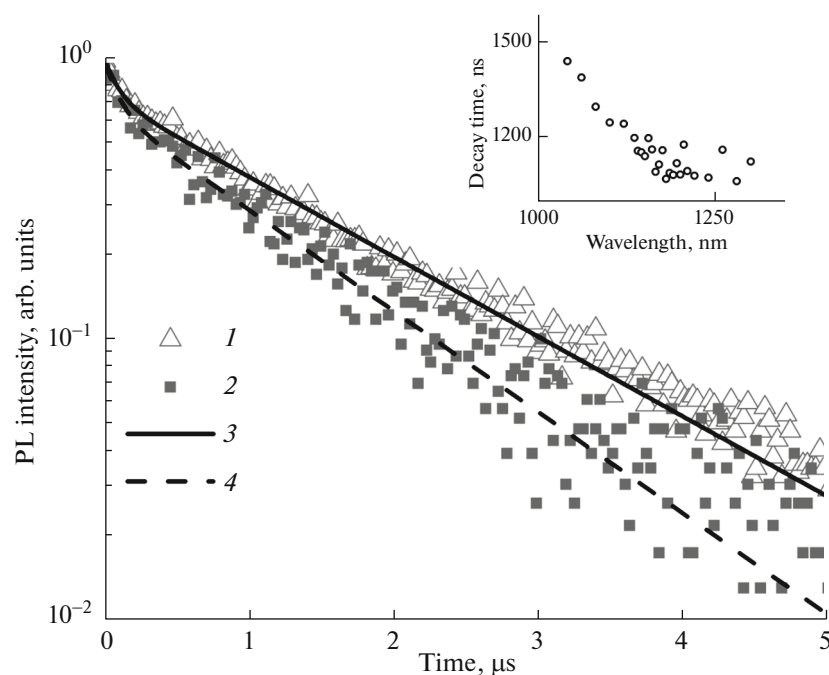


Fig. 5. Decay curves for PL detected at the wavelengths 1040 nm (1) and 1240 nm (2); (3) and (4) stand for biexponential decay fit for (1) and (2), respectively. Inset: averaged decay times spectrum.

APD have been previously described in [7]. The decay curves obtained for the samples described above are shown in Fig. 4. We obtained very good signal-to noise ratio with incredibly short acquisition time: 3 minutes. Resulting curves can be fitted well with exponential decay functions.

A high performance of the experimental setup makes it possible to perform spectrally-resolved PL decay analysis. Figure 5 shows the spectral dependence of the PL decay times obtained for PbS QD's in tetrachloromethane.

CONCLUSIONS

To summarize, we built the experimental setup for the NIR PL measurements, which operates in both steady-state and time-resolved modes in a spectral range from 900 to 1700 nm with high temporal resolution. The setup allows to carry out spectrally-resolved PL decay analysis and to investigate temperature dependencies of PL parameters. The performance of the setup is illustrated using PbS QDs monolayer and highly-diluted colloidal solution.

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