Colloidal quasicrystal for photonics

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Abstract In this work a method of the laser synthesis of colloidal nanoparticles and the formation of liquid photonic crystals are discussed. Optical properties of the systems depending on the particle concentration, its sizes and shapes were determined.

1. Introduction
At present there is the great deal of research related to the application of semiconductor quantum dots having the optical transitions in the visible range of the spectrum. Nowadays more and more attention is paid to nanocrystals of lead chalcogenides (PbS, PbSe, PbTe) – narrow-gap semiconductor compounds with a band gap of 0.41, 0.278 and 0.31 eV at 300 K with transitions, occupying a wide range of near-infrared region of the spectrum (0.8-5 microns) [1-2].

Colloidal quantum dots are the best alternative to conventional various organic and inorganic fluorophores which are good at not only in photostability, but also on the molar extinction coefficient, and having a number of unique photophysical properties. Semiconductor quantum dots located inside complexes with the nanoparticles (NPs) of noble metals or carbon chains can be used in a varied applications such as sensor systems and optoelectronic devices [3-4].

2. Laser synthesis of colloidal systems
The semiconductor nanoparticles were prepared by using laser ablation in a liquid under the radiation of a continuous laser beam (wavelength is 1.06 μm; power density is about 105W/sm2) [5]. In this case the photon energy of laser quantum is much greater than the band gap of used semiconductors. The radiuses of the produced nanoparticles (d, nm) were determined by using a particle size analyzer 550 Horiba LB-550, the functioning principle of which is based on the effect of dynamic light scattering. Physics of quantum dots creation for lead chalcogenides materials associate with the value of the Bohr radius of the exciton \( a_B \), which is defined as:

\[
    a_B = \frac{\hbar^2 e^2}{\epsilon \epsilon_0 m^*},
\]

where \( \hbar \) – is the Planck's constant, \( \epsilon \) – the high-dielectric constant of material, \( e \) – is the electronic charge, \( m^* \) – the effective mass of the exciton, which is calculated through the effective masses of electrons \( m_e^* \) and holes \( m_h^* \):

\[
    \frac{1}{m^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}.
\]
Because of the fact that the lead chalcogenides have large values of high-frequency dielectric constant and small values of the effective masses of electrons and holes, the exciton Bohr radius is large value calculated for the isotropic case, for example for PbTe it is about 50 nm.

The comparison of the NPs size with the exciton Bohr radius shows that for nanocrystals of lead telluride, the strict condition is right (see figure 1). So, for PbTe anoparticles the size quantization conditions are realized. The result is there are energy gaps in the electronic spectra of the quantum dots, which can significantly exceed the value of the band gap of the bulk lead chalcogenides.

![Figure 1. Images of PbTe NPs as a regular polygons: a) clusters of nanoparticles were fixed by atomic force microscope Ntegra Aura. The concentration of a colloidal solution was 1μg/ml, b) a single NP and its diffraction pattern is shown in the top right corner. The estimated period of the lattice constant ≈ 0.64 nm.](image)

The quantum dots of PbTe/PbSe were quasiperiodically distributed in a volume of a viscous liquid medium by the effect of self-organization: the compensation between the Coulomb repulsion and van der Waals attraction. The scheme of the diffraction pattern monitoring at the action of laser illumination of the liquid quasicrystal by visible range λ = 520 nm(see fig. 2). To reduce the thermal noise, a cell with a liquid was cooled down to 0 °C and was placed on a heat stabilized table. The temperature was measured by a contact less method using the IR thermometer Testo 830-T2. Fourier transform of the diffraction pattern confirms the presence of sensible and latent period in distribution of the semiconductor NPs in photonic liquid crystal.
3. Properties of liquid systems

The experiments to study the effects of the interaction of an electromagnetic radiation with intensity range from 102 to 104 W/cm² with a liquid photonic crystal were performed. The systems may be applied in IR fiber optics. However, in our case the fluorescence intensity is insufficient for stable manifestations of optical effects due to the low concentrations of NP semiconductor in colloidal systems. A presented decision is the using Purcell effect by creating complexes including metal and semiconductor particles. We have used PbTe system in combination with NPs Au (the average size was about 10 nm, see fig. 3a) because the effect of increasing the absorption of the semiconductor quantum dots in the presence of plasmonic nanoparticles was well reproduced. FTIR-spectroscopy was used to analyze changes in properties of colloidal systems by the absorption spectra (see fig. 3b). The stable increasing of an absorption for the complex systems are fixed.
The distance between the semiconductor quantum dots and metal nanoparticles is a key factor that affects the efficiency of exciton-plasmon interactions between them. When the quantum dot lays closely to the particles, the mechanism of non-radiative relaxation of the exciton quantum dot to the surface of the metal nanoparticles can be realized. There is a decrease in the fluorescence quantum yield of the quantum dot. On the other hand, when the quantum dot is located a far from the nanoparticles, the fluorescence quantum yield is also reduced. As the induced optical field of plasmon nanoparticles decays rapidly with distance from its surface. Thus, only at distances comparable to the particles size the efficiency the exciton-plasmon interactions between quantum dots and metal nanoparticles would be optimal [6].

Figure 4. The fluorescence spectrum of semiconductor-metal complexes in different mass proportions, distributed in the volume of glycerol. The wavelength pumping was 488 nm.

The luminescence time of complex PbTe-Au decrease up to $t = 2.3 \times 10^{-9}$ s in comparison to initial PbTe liquid system $t = 1.4 \times 10^{-8}$ s. It is connected the develop of the Purcell effect in media without strong separation boundary metal-semiconductor and quasiperiodically distribution of elements.

4. Conclusion

The results of the quasiperiodical forming of liquid systems on semiconductor quantum dots are shown in this work. Its optical properties depending on the parameters of the colloidal system were investigated. The fluorescence of the colloidal system of metal-semiconductor systems PbTe - Au in the visible spectrum was detected. The concentration of gold nanoparticles in a colloidal system affects to the manifestation of this effect.

Raman and FTIR-absorption spectra were measured at Center for Optical and Laser Materials Research, St. Petersburg State University.

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