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Electron-phonon interaction in composites with colloidal quantum dots: a study by luminescence spectroscopy and Raman scattering

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The temperature-dependent luminescence spectra were analyzed to determine the parameters of the electron-phonon interaction (Huang-Rhys factor and the average phonon energy) for nanocomposites with colloidal CdSe/CdS/ZnS quantum dots (deposited on the surface of a glass substrate and embedded in a thin polymer film of polyisobutylene, and in a frozen colloidal solution in toluene). The measured values of the parameters are analyzed in comparison with model calculations and data obtained using the low-frequency Raman spectroscopy. It is found that in the case of a vitrified colloidal solution of quantum dots in toluene, the matrix effect leads to a noticeable change in the parameters of the electron-phonon interaction.

Keywords: quantum dot, nanocomposite, polymer, phonon, electron-phonon interaction.

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Introduction

Modern photonics and its various interdisciplinary applications require solving a wide range of problems, among which a special place is occupied by the engineering of new nanostructured materials with given (controlled) properties and the development of methods for studying such systems [1]. One of unique new materials, that become the basis of more and more new technologies, are semiconductor nanocrystals (quantum dots, QDs). The study of photophysical properties and internal dynamics of nanocomposites based on QDs [2] has become an urgent fundamental task in this area. Significant efforts are currently directed towards the search and study of new luminophores [3] and suitable solid-state matrices for the synthesis of QD-based functional materials, for example, polymers [4], liquid crystals [5], hybrid structures [6].

Quantum dots have a number of specific photophysical and spectral properties, which are determined by their structure, size, and microscopic features of interaction with the medium. The combination of these properties determines the wide range of QDs application in physics, materials science, biology, and medicine [7]. The development of new materials based on QDs requires studying the dynamic processes in QDs at a fundamental level, while the search for new luminescent labels is associated with clarifying the question of the ODs interaction with solid matrices, in particular, electron-phonon interaction [8–11]. One of the most effective methods for studying the dynamic properties of impurity solid materials is photon echo spectroscopy [12–14], however, classical luminescence spectroscopy, supplemented by temperature measurements, can also be effective in studies of this type [15]. The potential of this technique is significantly expanded when other experimental techniques are used together, in particular, low-frequency Raman scattering (RS), where the vibrational characteristics (phonons energy) can be measured directly [16].

Samples and study methods

We have previously studied samples that are thin layers of two-shell colloidal QDs CdSe/CdS/ZnS deposited on a glass substrate [14,17,18]. In the present paper we study the same QDs embedded in solid matrices: frozen toluene and polyisobutylene (PIB). Composites were fabricated using a highly concentrated solution of QDs CdSe/CdS/ZnS in toluene (96 mg/ml, manufactured by QD-Light, Russia). A thin PIB film was fabricated by centrifugation on a glass substrate made of mixture of polymer and QD solution, followed by the solvent removal in a vacuum oven.

In order to separate the contributions to the optical dephasing of the processes of QD interaction with the matrix and the processes inside the QDs themselves, we measured the luminescence spectra of the nanocomposites dependences on temperature. A semiconductor laser module with a wavelength of 515 nm and an output power of 200 mW was used as a radiation source for the samples luminescence excitation. The radiation was attenuated by neutral filters and focused on the sample using lens. To measure the luminescence spectra in the temperature range from 24 to 300 K, an RTI helium cryostat

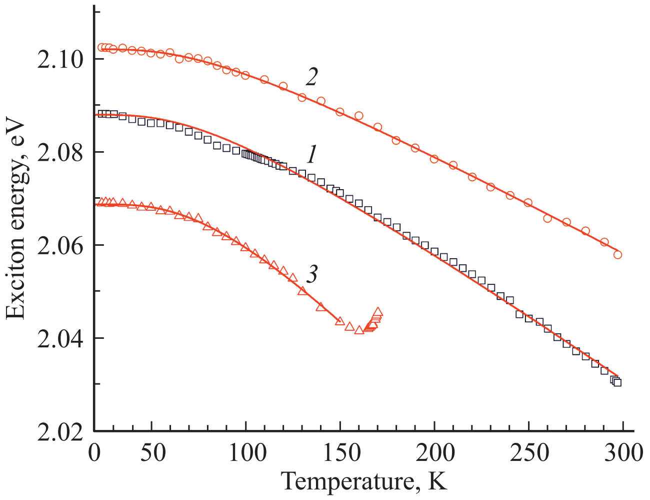

Figure 1. Temperature dependences of the maximum position of the luminescence spectrum (exciton energy) for nanocomposites based on QDs CdSe/CdS/ZnS deposited on the surface of glass substrate (*1*), embedded in PIB (*2*), embedded in frozen toluene (*3*) and their approximation (solid lines) using formula (2).

(Chernogolovka) was used. Using the Lakeshore DRC-91C temperature controller and the pressure regulation system for the cryostat measuring chamber precision temperature measurements were performed with minimum step of 0.2 K. The luminescence spectra of the samples were recorded using a compact fiber spectrometer (OtO Photonics, China).

Analysis of the luminescent spectra of nanocomposites with QDs dependent on temperature

For all samples, the luminescence spectra were measured over a wide temperature range. The spectra are symmetrical bands corresponding to exciton luminescence, with a width about 20–30 nm. Depending on the base matrix of the composite the spectra differed in the position of the peak maximum of the exciton luminescence (exciton energy). As the temperature was lowered, the maxima of the exciton bands in the luminescence spectra shifted to the UV region of the spectrum. Figure 1 shows the temperature dependences of the exciton energy for three QD samples CdSe/CdS/ZnS: deposited on the surface of glass substrate (curve *1*), embedded in polyisobutylene (curve *2*) and into frozen toluene (curve *3*).

The analysis of the literature has shown that for the first time the temperature dependence of the band gap for bulk semiconductors was empirically described by Varshni [19] in the form

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T}, \tag{1}$$

where $E_g(0)$ is the band gap at 0 K, α and β are parameters.

However, this relation is not very informative for studying the parameters of the electron-phonon interaction of QDs with matrix [20]. In O'Donnell and Chen paper [21] an analytical formula was derived to describe the dependence on temperature:

$$E_g(T) = E_g(0) - \frac{2SE_{LO}}{\exp(\frac{E_{LO}}{kT}) - 1}, \tag{2}$$

which contains additional parameters characterizing the strength of the electron-phonon interaction — S (Huang-Rhys factor) and the average phonon energy during relaxation of the electronic excitation E_{LO}.

By approximating the temperature dependences of the exciton energy obtained in the experiment by formula (2), we obtained the values of the parameters of the electron-phonon interaction for different samples with QDs (Table).

The obtained values of the band gap $E_g(0)$ are practically the same for all samples and correspond to the band gap for the bulk semiconductor and CdSe nanoparticles [22]. Studies show that the value of $E_g(0)$ can vary quite strongly depending on the QD concentration in a specific sample [23], and this circumstance must also be taken into account, since QDs are distributed differently inside different matrices. The band gap is related not only to the energy gap between the levels of the valence zone and the conduction zone for bulk semiconductor, but also to the size of the nanocrystals themselves. To determine the characteristic dimensions and composition of the QDs used by us, we carried out additional measurements using a transmission electron microscope (TEM, Center for Collective Use „Studies of Nanostructural, Carbon and Superhard Materials" FSBI TISNCM, Moscow). Based on the processing of images obtained with TEM, the statistics of the nanocrystals distribution by sizes d was made. Using the experimental data for the exciton energy dependence on size of QDs CdSe [24], the range of possible values of $E_g(0)$ was determined: 2.04–2.16 eV, which is in good agreement with the values of $E_g(0)$ obtained by approximation of the temperature dependences of the luminescence spectra of composites with QDs CdSe/CdS/ZnS.

The obtained values of the Huang-Rhys factor S are quite different for different samples, i.e. the presence of the surrounding matrix strongly affects the parameters of the electron-phonon interaction. S highest value was obtained for QDs embedded in toluene. This may be due to the effect of thermal expansion of solid toluene on the electronic-vibrational spectrum [20]. Besides, the high value of the Huang-Rhys factor may be associated with high concentration of QDs.

E_{LO} values for different samples also differ, which may indicate a noticeable hybridization effect of vibrational (phonon) modes, i.e. about the interaction of the emitting QD nucleus not only with local QD phonons, but also with matrix phonons. Solid matrices used for samples preparation are characterized by their own phonon spectrum, which leads to differences in the average energy of phonons E_{LO} localized inside the QDs. Differences in the parameters of the

Electron-phonon interaction parameters for nanocomposites with QDs CdSe/CdS/ZnS, calculated from the analysis of temperature-dependent luminescence spectra and RS spectra

Sample	$E_g(0)$, eV	S	E_{LO}, cm^{-1}	Line frequency in RS spectrum, cm^{-1}
QD/PIB	2.10 ± 0.02	1.31 ± 0.02	170 ± 3	206.1 ± 0.2
QD on glass	2.09 ± 0.02	1.67 ± 0.02	172 ± 4	205.5 ± 0.2
QD/toluene	2.07 ± 0.02	2.66 ± 0.10	183 ± 5	–

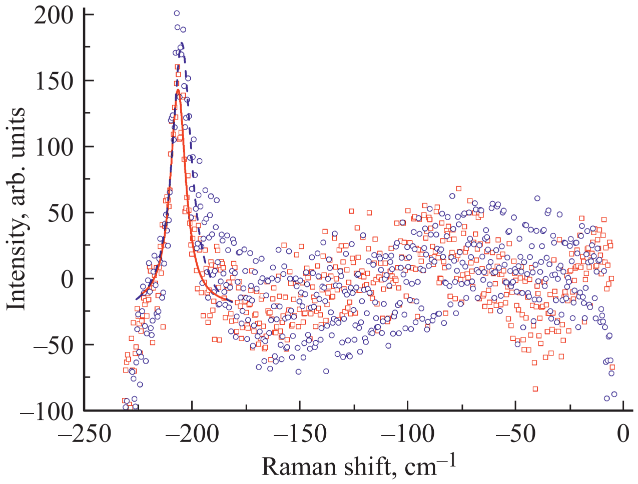

Figure 2. RS spectra (anti-Stokes component; after background subtraction) for QDs CdSe/CdS/ZnS on glass substrate (red squares) and QDs embedded in PIB (blue circles) measured at room temperature. The solid and dashed lines show the results of data approximation by the Lorentz function.

electron?phonon interaction lead to a noticeable change in the effective frequency of the local phonon, which indicates a strong influence of the matrix dynamics on the spectral and luminescent properties of QDs. The last conclusion is confirmed by the behavior of the temperature dependence of frozen toluene near the glass transition temperature (165 K). The nature of the temperature dependence changes drastically, i.e., the anomalous dynamics of the matrix under the conditions of the phase transition begins to play the main role.

The analysis of temperature-dependent luminescence spectra is an indirect method for obtaining information about the parameters of localized phonons. To confirm the obtained data, we carried out additional measurements by the RS method. Low-frequency RS spectra in the range from 6 to 230 cm^{-1} for a thin layer of QDs on substrate and QDs embedded in PIB (Fig. 2) were measured at room temperature on TriVista 777 spectrometer using Millenia (532 nm) solid-state laser at the IAE SB RAS. Ambient light from the laser was suppressed using monochromator [25] (see detailed description of method used for low-frequency RS spectroscopy in, for example, [26]). For the studied samples, bands were found in RS spectrum in the region of 205–206 cm^{-1}, which is in good agreement with the estimates of E_{LO} value by the luminescence spectra. Additional information about the matrix effect on the vibrational spectra of nanocomposites can be obtained from energy measurements of not only longitudinal (LO), but also transverse TO-phonon modes [27]. For shells made of wide-gap semiconductor CdS and ZnS, organic ligands, and the surrounding polymer matrix, these components are in a different frequency range. Besides, hybridization of phonon modes can occur [28].

The parameters obtained from the analysis of the temperature-dependent luminescence spectra of nanocomposites with colloidal QDs are in good agreement with model calculations and the results of other studies, which indicates the adequacy of the model selection and the reliability of the data obtained.

Conclusion

For composites based on colloidal QDs CdSe/CdS/ZnS in wide range of low temperatures (from 24 to 300 K), the temperature dependences of the luminescence spectrum position related to the exciton energy and band gap were measured. Within the framework of the electron-phonon interaction model, the energy values of localized phonons and the Huang-Rhys factor are determined. The specified parameters are found for three systems: QDs deposited on the glass surface by the blade application method, thin polymer (PIB) film with embedded QDs, thin (about 1 mm thick) layer of frozen (vitrified) colloidal solution of QDs in toluene. A noticeable difference in the parameters was found for QDs in frozen toluene, which may indicate the effect of mode hybridization. In the same sample an anomalous temperature behavior was revealed near the glass transition temperature of the sample. The results obtained by the luminescent spectroscopy methods correlate well with the data of low-frequency Raman scattering in the same materials. The developed approach makes it possible to study the matrix effect on the spectral and photophysical properties of nanocomposites.

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Conflict of interest

The authors declare that they have no conflict of interest.

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