



Relation between excitation dependent luminescence and particle size distributions for the selenium nanoparticles in κ -carrageenan shell

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ABSTRACT

In this paper synthesis and optical properties of selenium nanoparticles in κ -carrageenan shell were study. It was found excitation-dependent luminescence of the κ -carrageenan-Se nanoparticles. This luminescence is caused by quantum confinement effect. The nanoparticle size distribution was estimated using optical absorption and luminescence spectra. The distribution are agree well with the one obtained by transmission electron microscopy.

1. Introduction

In recent times, selenium nanoparticles (SeNPs) and nanocomposites based on them are attracting increased attention of researchers in different areas of science and technology [1–3]. Such research activity led to the replacement of earlier used simple extremely toxic inorganic compounds of the selenium [4] and bulk-selenium [5] by modern environmentally friendly materials (including nanomaterials) with a set of promising properties and the possibility of their application in such strategically important industries as biomedicine [6], electronics [7], photonics [8]. In particular, there are many examples of successful using of the SeNPs as an auxiliary agent for the anticancer therapy [9] and cancer diagnosis [10], transistor and solar cells [11], highly effective low-toxic antioxidant [12] and antiviral drugs [13]. In addition, the fluorescent ability of very small SeNPs allows to use them as quantum dots emitting near the transparency window of biological tissues [14]. It is known that the ultradispersity of particles causes the manifestation of specific “size effects”, and, accordingly, a strong relationship, in particular, between the most important parameters of fluorescence and the main nanomorphological characteristics (particle size, degree of polydispersity, shape of particles and their ligand environment) [15]. Therefore, determination of the composition and size characteristics of the synthesized nanoparticles can be predict potential ways of these application.

At this moment several methods exist to estimate the size of nanoparticles. High-resolution transmission electron microscopy allows to directly visualize the particles and determine their size distribution and

shape. Also often used in practice are the methods of RDA, DLS and SLS. They allow to determine the average size of nanoparticles and in some cases their shape can be estimated. However, these methods require expensive equipment and consumables, as well as complex sample preparation (ultrafiltration etc.). Therefore, described methods are relatively expensive for express-evaluation and control of the size characteristics of SeNPs. The fluorescence capacity and the expressed spectrum of optical absorption of SeNPs allow to involve spectroscopic methods for the characteristic of their size and disperse distribution.

We study water-soluble nanocomposites consisting of Se-NPs stabilized by κ -carrageenan (κ -CG). The κ -CG is a biocompatible natural sulfated polysaccharide extracted from red algae and possessing a complex of biological activity: membranotropic effects [16], anti-diabetic activity [17], anticoagulant properties [18]. It is widely used in the food and cosmetic industries [19,20]. Early we have synthesized a number of nanocomposites with nanoparticles of silver [21,22] and gold [23], quantum dots of cadmium selenide [24] and struvite-dittmarite complex mineral on the base of κ -CG [25].

The luminescence of amorphous selenium has been studied for a long time [26–28]. However, the particles of small size for a long time could not be obtained due to the rapid aggregation. Nevertheless, SeNPs with a size of 10 nm were obtained. The luminescence shift observed in this material was due to quantum confinement [29]. Earlier [21,30], it was found that polysaccharide is a good shell for nanoparticles, which prevents their clustering. In this paper, we study the luminescence properties of SeNPs capped with κ -CG in water.

An important task in the study of nanoparticles is to obtain their size

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distribution. Ultradispersity of particles causes the manifestation of specific “size effects” and a strong relationship between biological properties and morphological parameters such as diameter of nanoparticles, their polydispersity, shape and ligand environment [15]. It was found [31] that the size of quantum dots directly determines their toxicity. Quantum dots of smaller size actively penetrate into the cell into the cytoplasmic space, as well as into cell organelles (mitochondria, lysosomes, Golgi complex and nucleus). Small quantum dots trigger the processes of autophagy and apoptosis better than larger ones due to interaction with these life-supporting cellular structures, that leads to cell death and causing its high toxicity. A similar dependence of the toxicity of nanoobjects on their size is also demonstrated in the review paper [32]. Therefore, control of nanoparticle size distribution is very important in synthesis of nanoparticles for biological and medical application. Often, the average size of nanoparticles is estimated by the energy of the fundamental absorption edge, however, due to its broadening, this presents some difficulties [33]. In this paper, we estimated the particle size distribution from the luminescence spectra and compared the results with other optical methods and TEM.

2. Methodology

2.1. Synthesis

Powder selenium, potassium hydroxide and hydrazine-hydrate were purchased from Reachim (Russia). The κ -carrageenan (κ -CG) (MW 1100 kDa) was purchased from CP Celco (Denmark). All chemicals were used as received without additional purification.

SeNPs-containing nanocomposites ($\text{Se}^0/\kappa\text{-CG}$) were prepared by the method described in detail in Refs. [34,35]. Briefly, in a three-necked flask equipped with a reflux condenser and a thermometer, 0.284 g KOH and 1 ml $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ were placed under constant stirring, then the temperature of this reaction medium was brought to 70 °C and 0.16 g of elemental bulk-selenium was added with continuous argon flow. The synthesis time was about 30 min. The formation of highly reactive Se^{2-} -anions is accompanied by the appearance of a characteristic red-maroon staining and complete dissolution of selenium. Next, an aliquot of the obtained reaction mixture containing Se^{2-} -anions ($V = 0.02\text{--}0.05$ ml) was added to the previously obtained κ -CG solution (1.0 g κ -CG in 80 ml water) and stirred at room temperature for 20 min. The isolation of the target nanocomposites and their purification from impurities were performed by precipitation with a fourfold excess of EtOH, followed by repeated washing with ethanol and drying in air at room temperature. The content of Se^0 in the obtained nanocomposites was 0.3 and 0.6% by mass yield 89–94%.

2.2. Characterization techniques

FTIR spectra were recorded by a FTIR Bruker Vertex 70 spectrometer in KBr pellets in the range $4000\text{--}400\text{ cm}^{-1}$. ^{13}C NMR spectra of the solutions in D_2O (concentration was 2%) with addition of copper acetate as relaxant at 27 °C were measured by a Bruker DPX-400 spectrometer operating at 100.13 MHz. The chemical shifts of all carbon atoms are reported relative to DSS internal standard ($\delta = 0.000$ ppm). There are ^{13}C NMR signal of κ -CG located at δ : 104.7 (C-1 G4S1), 97.0 (C-1 DA2), 71.7 (C-2 G4S), 80.7 (C-3 G4S), 81.5 (C-3 DA), 76.0 (C-4 G4S), 80.6 (C-4 DA), 77.0 (C-5 G4S), 78.9 (C-5 DA), 63.5 (C-6 G4S) ppm.

X-ray diffraction study was carried out on a Bruker D8 ADVANCE X-ray diffractometer under monochromatized $\text{Cu-K}\alpha$ radiation. Transmission electron microscopy (TEM) measurements were performed by a Leo 906 E microscope operated at an accelerating voltage of 120 kV. The size distribution of nanoparticles was determined by statistical processing of TEM microphotographs. The elemental compositions were determined with a Thermo Scientific Flash 2000 CHNS analyzer and by X-ray energy dispersive microanalysis with a Hitachi

TM 3000 scanning electron microscope equipped with a SDD XFlash 430-4 X-ray detector. The sulfatation degree of κ -CG and its nanocomposites was determined by elemental analysis according to the ratio of sulfur to carbon, hydrogen, and oxygen contents. The following concentrations of elements (C 33.1%, H 6.1%, S 6.8%, Na 3.36%, K 3.6%) in κ -CG composition were determined by elemental analysis.

2.3. Optical spectroscopy

All measurements were performed on water solution of SeNPs placed into quartz cuvette. The optical absorption spectra were obtained by a Perkin-Elmer Lambda 950 UV/VIS/NIR spectrophotometer. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of water solution SeNPs were obtained with a Perkin Elmer LS-55 instrument. Spectral widths of excitation and emission slits were 15 nm and 10 nm. All PLE spectra were recorded using the wavelength of the PL maximum as the monitored wavelength. PL spectra are presented with spectral correction for response of the detection channel in the measured spectral range. PLE spectra were corrected for the varying intensity of exciting light due.

PL quantum yields of SeNPs solutions were measured using the comparative method of Williams [36] with reference standard sample of methylene blue with known quantum yield $Q_R = 0.52$ [37,38]. PL spectra of water solutions containing different concentrations of SeNPs were recorded together with absorption spectra. Dependence of integrated PL intensity vs absorbance were plotted. The result was a straight line with gradient m . Similar procedure was performed for solutions with different concentrations of the reference sample. The result was a straight line with gradient m_R . Therefore, quantum yield Q of SeNPs can be calculated using the following equation:

$$Q = Q_R \frac{m}{m_R} \quad (1)$$

The error in the reported value must be considered based upon the observed errors in the gradients.

3. Results and discussion

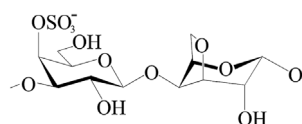
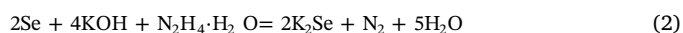
3.1. Samples characterization

According to FTIR-, ^{13}C NMR spectroscopy [39–41] and elemental analysis, the κ -CG composition consists of regularly alternating residues of 3-O-substituted β -D-galactopyranose with the sulfate group substituent in the position 4 and the 4-O-substituted 3,6-anhydro- α -D-galactopyranose according to Scheme 1.

The degree of sulfatation is about 6% and it corresponds to one sulfate group on the macromolecule κ -CG disaccharide unit. Its molecular weight is high ($M_p = 631.1$ kDa, $t_r = 29.4$ min, $M_w = 1009.0$ kDa, $M_n = 564.7$ kDa), a molecular mass distribution is broad, and the polydispersity index is about 1.79 [23,40].

The nanocomposites $\text{Se}^0/\kappa\text{-CG}$ (SeNPs) with a selenium content 0.3% (Sample 1) and 0.6% (Sample 2) were synthesized by oxidation Se^{2-} to Se^0 in the κ -CG's water solution.

Se^{2-} ions were obtained previously by reduction of elemental bulk-selenium by hydrazine hydrate in an alkaline medium. As a result the selenium is dissolved, and the highly reactive selenide anions are formed according to equation (2):



Scheme 1. The chemical structure of κ -CGs unit.

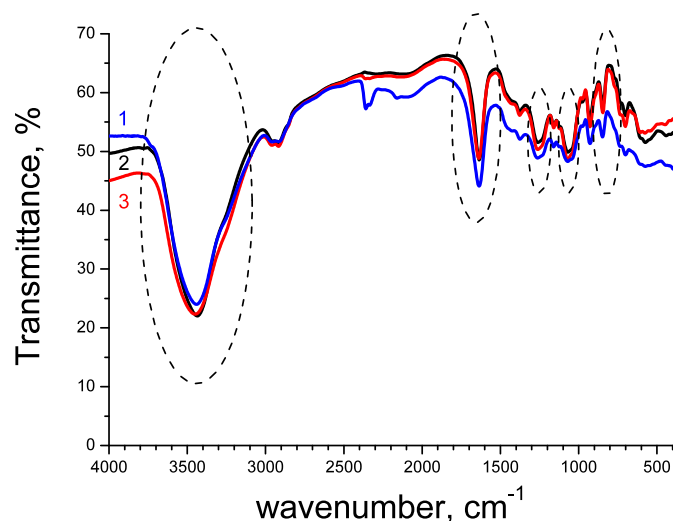


Fig. 1. IR-spectra of κ -CG (curve 1) and SeNPs: Sample 1 (curve 2) and Sample 2 (curve 3).

Generated Se^{2-} ions are characterized by limited time stability. After injecting them into the κ -CG aqueous solution, selenide-anions are oxidized by molecular oxygen in the κ -CG aqueous solution to elemental selenium with followed by coalescence of Se^0 ions into nanoparticles. Passivation of the SeNP energy-saturated surface and security their aggregative stability occur due to adsorption of polysaccharide macromolecules on the SeNPs surface (steric stabilization), as well as the electrostatic stabilization of the surface by the highly polar κ -CG macromolecule functional groups (hydroxyl-, carbonyl-, sulfo-groups). Wherein, a single hybrid stable water-soluble system of “nanonucleus Se^0 -polysaccharide shell” is formed.

The participation of κ -CG functional groups in the stabilization of the formed SeNPs is confirmed by the data of FTIR-spectroscopy. Bands in the FTIR-spectra of native κ -CG are characterized polysaccharide structure (Fig. 1). The strong and wide band at 3441 cm^{-1} belonged to the O–H stretching vibration of the polysaccharide, and the relatively weak absorption peaks at about 2958 and 2915 cm^{-1} were due to C–H stretching vibration. The band at 1636 cm^{-1} was due to O–H bending vibration. The band in the range of 928 – 1229 cm^{-1} was assigned to C–O antisymmetric stretching in the C–O–H or C–O–C groups of polysaccharides. A band located in the region of 1263 cm^{-1} corresponds to the total content of SO_4^{2-} . Low intensity of this band is due to low-sulfation of this sample.

Band in the region of 845 cm^{-1} corresponds to C–O–S vibrations of the secondary axial sulfo-group at C-4 β -D-galactopyranose. Whereas, position of the band and their intensity are slightly changed in the SeNPs-containing nanocomposites in comparison with the native κ -CG. In particularly, a shift band and a decrease in its intensity are observed in the region of 3436 cm^{-1} , as well as a shift and an increase in the intensity of the bands were found in the region of 1068 , 1260 and 845 cm^{-1} . These facts can be explained by a direct participation of hydroxyl, ester and sulfo-groups in the electrostatic stabilization mechanisms of the formed SeNPs [42].

All of the obtained Se^0/κ -CG nanocomposites are amorphous. It was determined by XRD. The diffraction pattern completely repeats the one of the original κ -CG polysaccharide matrix. The absence of reflections corresponding to the crystallographic planes of crystalline Se^0 (hexagonal, trigonal, rhombic, and monoclinic) probably indicates the formation of an amorphous modification of selenium, and did not allow to determine the average size of SeNPs by XRD method.

According to data of TEM, Se^0/κ -CG nanocomposites are formed as nanoparticles of approximately spherical shape dispersed in a κ -CG polysaccharide matrix (Fig. 2, a and c). Diameters of Se-NPs vary between 1.5 and 8.5 nm for Sample 1 and 2 – 11 nm for Sample 2. On the

diagram of the nanoparticles dispersed distribution for Sample 1, one maximum corresponding to the size range of particles 2.5 – 5 nm is found and mean particle diameter is about 4.6 nm (Fig. 2, b). Whereas in the diagram for Sample 2, two distributions with mean diameters 4.5 and 8 nm appear (Fig. 2, d).

The broad size distribution of SeNPs in Sample 2 and the presence of two dimensional regions in the dispersion diagram is probably due to the difference in the synthesis conditions of nanocomposites. Sample 2 has higher concentration of Se^{2-} ions than Sample 1 in the reaction medium at the same κ -CG concentration in solution.

The formation of SeNPs in the κ -CG aqueous solution is a multistage complex process where four main stages can be selected [43,44]. The scheme of the process is presented in Fig. 3. At the first stage, the oxidation of previously synthesized highly reactive selenide anions occurs with the formation of selenium atoms. The second stage is characterized by oversaturation of the reaction medium with selenium, the formation of a metastable phase with its subsequent transition to a thermodynamically stable state and an increase of the local fluctuations level in the bulk of the initial phase. As a result the homogeneous spontaneous formation of ensembles of selenium atoms through their reversible association, the formation (after overcoming energy barriers) of the critical nucleus of a new phase takes place. At the third stage, the nuclei formed at the first stage grow due to sorption process. Nanoparticles are formed with subsequent steric and electrostatic stabilization by κ -CG macromolecules (fourth stage). The increase of the SeNPs polydispersity in Sample 2 and the ability to select two types of nanoparticles (small 4.5 nm and larger 8 nm) in the histogram of the size distribution (Fig. 2, d) can be explained by diffusion limitations of the mass transfer rate and nucleation of selenium atom ensembles during nanoparticle formation. Such restrictions are probably caused by a higher concentration of selenium precursor (K_2Se) in the composition of the reaction medium, which is accompanied by the interaction of potassium ions with κ -CG and an increase of the its aqueous solution viscosity and the difficulty of selenium atoms diffusion to the surface of growing nanoparticles.

3.2. Luminescence

Luminescence properties of solutions of SeNPs with κ -CG shell are studied. Emission spectra of two samples of SeNPs are given at different excitation wavelengths in Fig. 4. In Sample 1 (Fig. 4a), when the excitation wavelength is changed to the long-wave side (from 400 to 640 nm), the luminescence band maximum is also shifted from 520 to 760 nm (2.38 – 1.63 eV). There are typical series of excitation-dependent photoluminescence spectra [45]. Intensities of emission bands are not equal. First, there is an increase in intensity, and then a decrease. The most intense luminescence band peaked at about 620 nm (2.00 eV) is excited at 550 nm (2.25 eV).

In Sample 2, when the excitation wavelength is changed from 400 to 650 nm (3.10 – 1.91 eV), the maximum of the luminescence band is shifted from 550 to 750 nm . The most intense luminescence bands peaked at 610 nm (2.03 eV) and 695 nm (1.78 eV) are excited at 520 nm (2.38 eV) and 620 nm (2.00 eV), respectively.

The quantum yields for samples 1 and 2 are evaluated in comparison with the methylene blue solution with a known quantum yield using Eq. (1). The results are given in Table 1. The quantum yield of Sample 1 is about 4.7% . Sample 2 has 3.3% quantum yield.

In Fig. 5 the absorption and luminescence spectra of Sample 1 monitored in the 520 – 820 nm region are shown. A monotonic rise in the region of 3.0 eV is observed in the absorption spectrum. There are several bands in the excitation spectra. The position of the bands with maxima at the 4.5 and 3.4 eV does not depend on the observation wavelength, only their intensity changes. When the monitored wavelength is changed, a shift in the band from 2.95 to 2.5 eV is observed, and also a shift in the more intense band from 2.5 to 1.7 eV . In this case, the intensity of the band in the region of 2.5 – 1.7 eV increases with a

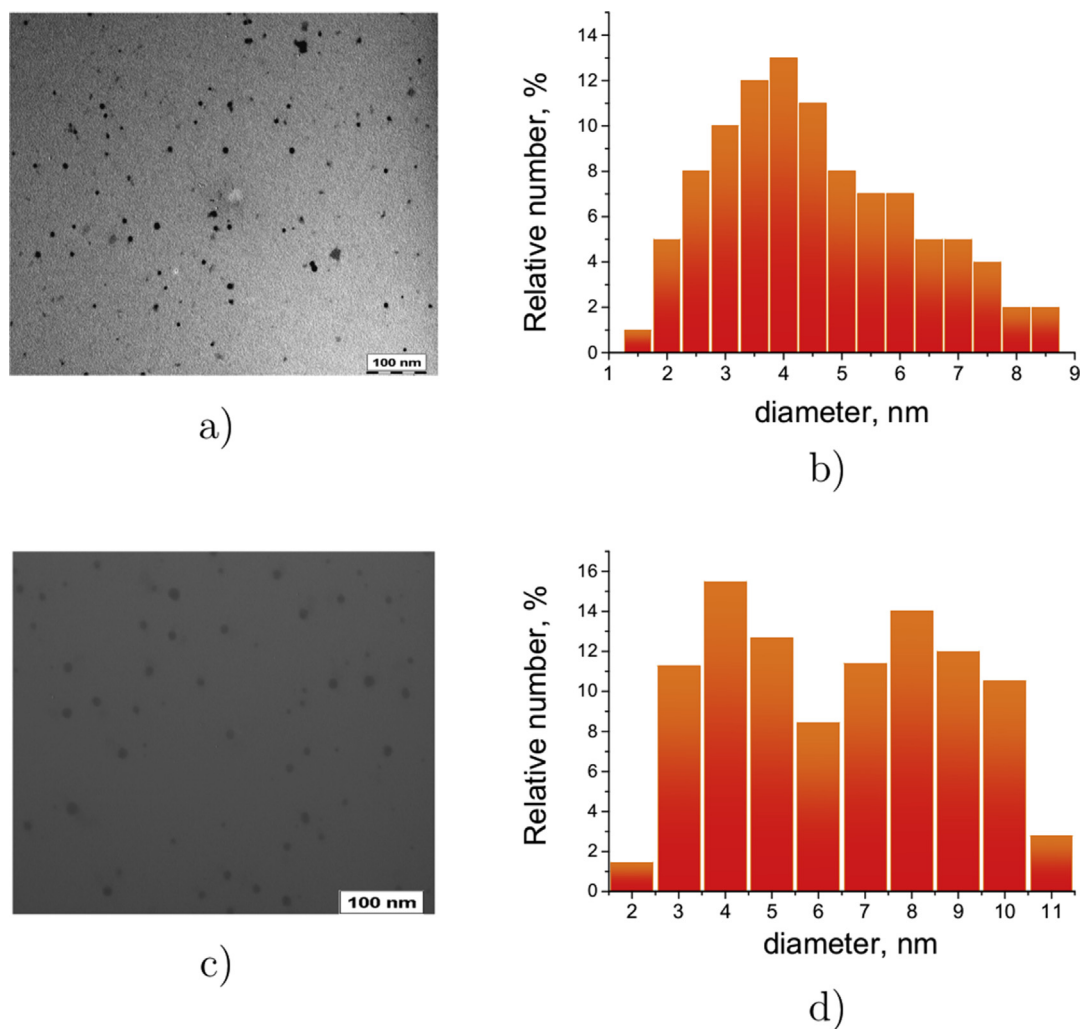


Fig. 2. TEM images and SeNPs diameter distributions of Sample 1 (a and b) and Sample 2 (c and d), respectively

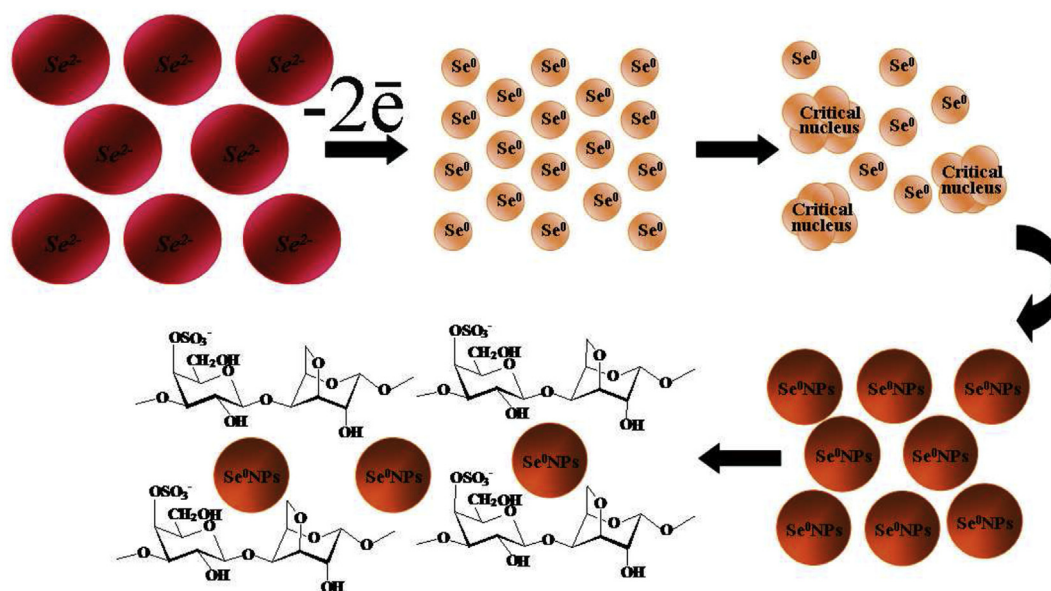


Fig. 3. The predicted scheme of $\text{Se}^0/\text{k-CG}$ nanocomposites synthesis.

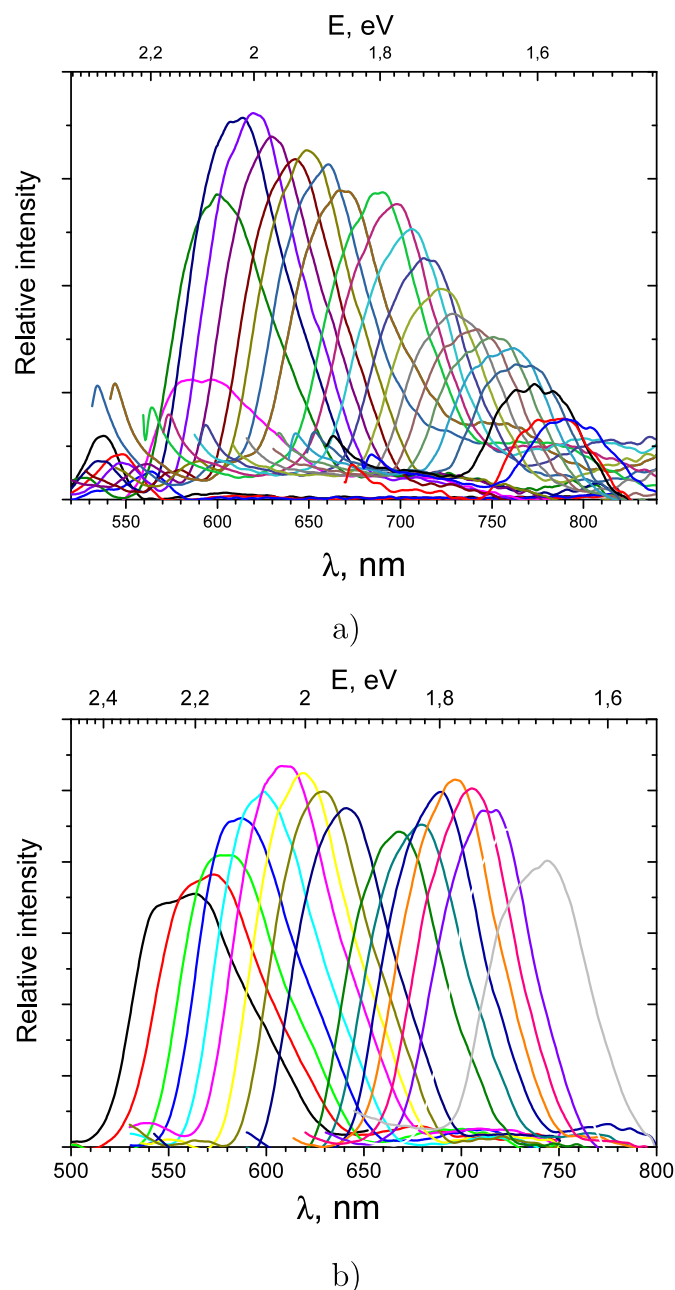


Fig. 4. Photoluminescence spectra of SeNPs in samples 1 (a) and 5 (b) under different excitation wavelength (from 400 to 650 nm).

shift in the monitored wavelength, and then decreases. The most intense band is observed at the monitored wavelength in the region of 620 nm (2.0 eV). The intensity of the band in the region of 3.0–2.5 eV monotonously decreases when the excitation wavelength is shifted to the long-wavelength region, similar to the intensities of bands with maxima of 4.5 eV and 3.35 eV.

In Fig. 6 the absorption and luminescence spectra of Sample 2 monitored in the 580–760 nm (2.14 eV–1.63 eV) region are shown. In the absorption spectrum, a monotonic rise is observed in the region of 2.8 eV. The excitation spectra are similar to Sample 1 in the behavior of the spectra.

Assuming that the rise in the absorption spectra of Samples 1 and 2 corresponds to the region of the fundamental absorption edge of SeNPs, one can estimate their bandgap. As shown above, nanoparticles have a certain size distribution. Therefore, the band gap determined from the absorption spectrum has the meaning of a certain mean band gap along

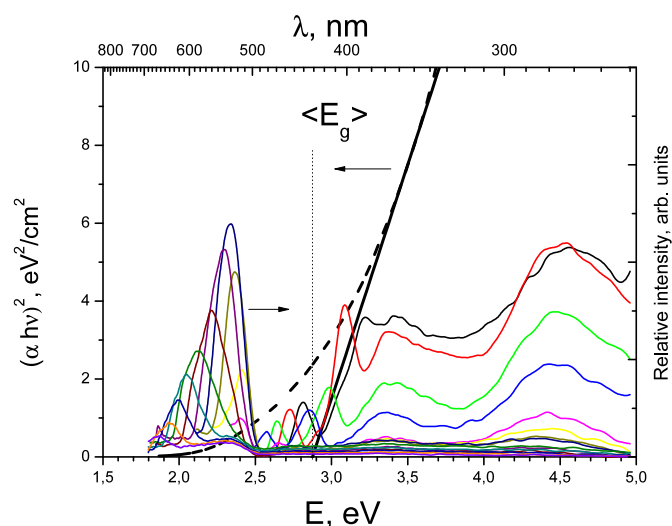


Fig. 5. Excitation spectra measured at different monitored wavelengths (520–820 nm) and absorption spectrum in Tauc plot of Sample 1 (dashed curve).

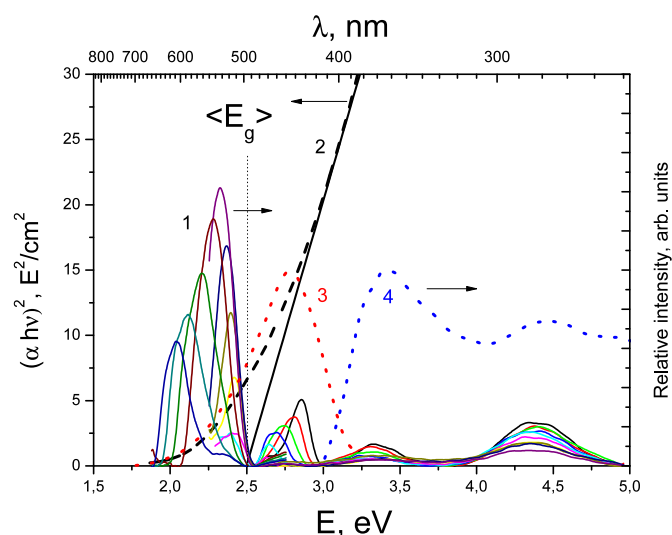


Fig. 6. Excitation spectra at different monitored wavelengths between 580 and 760 nm (group of curves 1) and absorption spectrum in Tauc plot of Sample 2 (curve 2 dashed curve). Dotted curves are related to luminescence (curve 3) and excitation (curve 4) spectra of κ -CG solution in water.

the ensemble of SeNPs ($\langle E_g \rangle$). For Sample 1, the mean band gap is about 2.87 eV, for Sample 2, it is about 2.5 eV (see Table 1).

In Fig. 6, curves 3 and 4 show the luminescence and excitation spectra of an aqueous solution of κ -CG. In the excitation spectrum of luminescence peaked at 2.75 eV, two bands are observed at about 3.4 and 4.5 eV. The found luminescence corresponds to singlet-singlet transitions in κ -CG [46]. Thus, the bands in the region of 3.4 and 4.5 eV in the excitation spectra of Samples 1 and 2 are also attributed to the excitation of transitions in the κ -CG shell of SeNPs.

Fig. 7 shows the luminescence, excitation and absorption spectra of a colloidal aqueous solution of amorphous Se without a κ -CG shell. In the emission spectrum (curve 1), a peak with a maximum in the region of 1.55 eV (800 nm) is observed. The excitation spectrum of luminescence at 800 nm is shown in curve 2. The spectrum clearly shows three bands with peaks at 1.87, 2.35 and 2.55 eV. In the absorption spectrum in the region of 2.0 eV, a sharp rise corresponds to the fundamental absorption of amorphous selenium. The absorption band can be used to estimate the width of the band gap $\langle E_g \rangle$, it is approximately 2.03 eV,

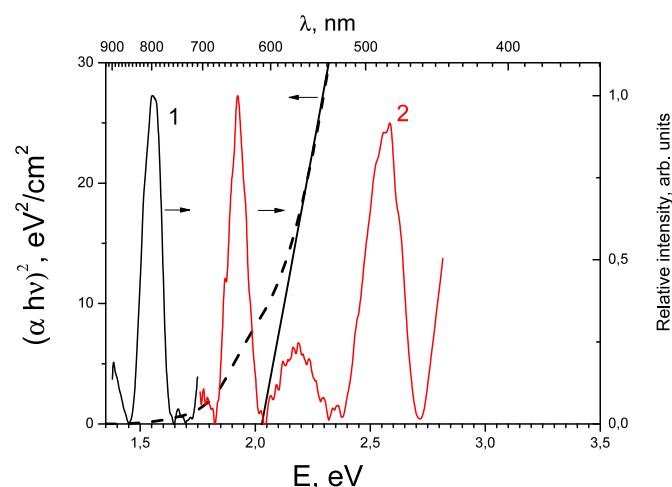


Fig. 7. Emission (curve 1), excitation (curve 2) and absorption spectra (dashed curve) of amorphous Se water solution.

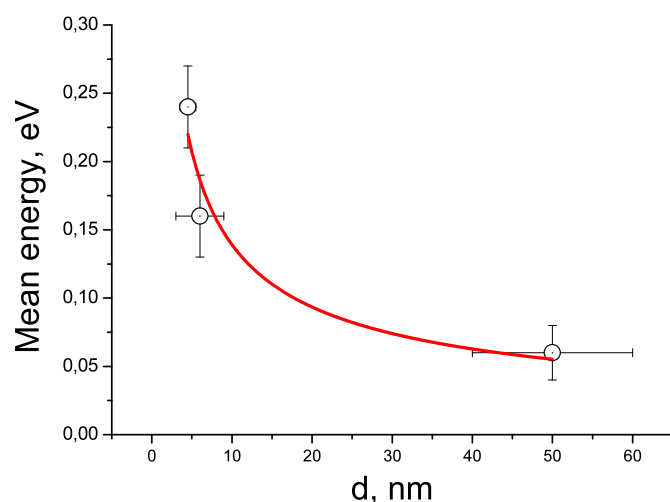


Fig. 8. Dependence of mean exciton binding energy on mean diameter of nanoparticles estimated from absorption spectra on Figs. 5 and 6. Solid curve is fitted by $E_b \sim 1/d^{0.57}$.

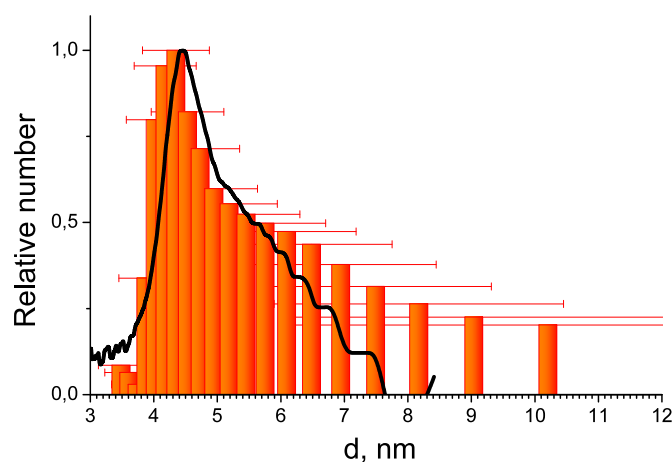
which is consistent with given in Refs. [47,48].

The observed luminescence in the 1.55 eV region is attributed to the exciton emission in amorphous selenium [28,48,49]. Thus, the excitation band at 1.87 eV corresponds to the transition to the first excited state of an exciton, whereas high-energy bands can be associated with higher-energy exciton states. In the model of a weakly bound exciton [50], the band gap is:

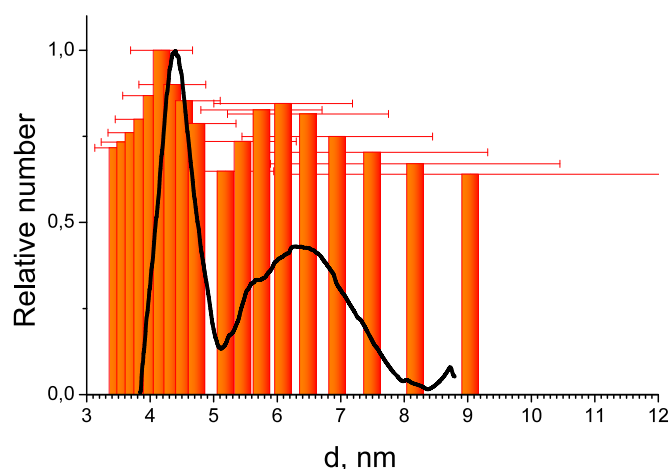
$$E_g = E_{ex} + E_b, \quad (3)$$

where E_{ex} is the energy of the lowest excited state of an exciton, and E_b is the exciton binding energy. The energy of the lowest excited state of an exciton is assumed to be equal to the energy at which the intensity of the excitation band in Fig. 7 decreases by a factor of two. There is 1.95 eV. Using the estimation for the band gap obtained above, we can calculate the binding energy of an exciton in amorphous selenium. It is 80 meV. It is in agreement with the previously obtained exciton binding energies in amorphous selenium in Refs. [26,27,51,52].

In a colloidal solution of selenium without a κ -CG, selenium particles quickly aggregate, forming particles of sufficiently large size on the order of several hundred nanometers. κ -CG forms a shell that prevents aggregation. The particle size of Se becomes much smaller, on the order of several nanometers according to TEM in Fig. 2. Therefore, the quantum confinement effect leads to an increase in the band gap [53].



a)



b)

Fig. 9. Distributions of SeNPs (Sample 1 (a) and Sample 2 (b)) size determined from intensity of emission spectra (columns) and equation (6) (solid line).

A shift of excitation bands attributed to an exciton state towards higher energies also occurs. Thus, the excitation bands in Figs. 5 and 6 can be interpreted as exciton excitation bands in SeNPs of various sizes. If we accept that the most intense excitation band corresponds to the lowest excited state of an exciton in mean-sized SeNPs, then from Eq. (3) we can calculate the mean exciton binding energy in nanoparticles $\langle E_b \rangle$ over the ensemble for Samples 1 and 2. For Sample 1, it is equal to 250 meV, while for Sample 2 it is equal to 160 meV. The results are given in Table 1.

The size of nanoparticles can be estimated in the approximation of an electron in a spherical quantum well developed by Brus [53]. The relationship between the band gap of the nanoparticle $\langle E_g \rangle$ and its radius r in this approximation is given by the following expression:

$$\langle E_g \rangle = E_g + \frac{\hbar^2}{8r^2} \left(\frac{1}{m_e^2} + \frac{1}{m_h^2} \right), \quad (4)$$

here m_e and m_h are effective electron and hole masses, E_g – is energy gap of amorphous Se. The effective electron mass is $0.25m_0$, and the effective mass of the hole is $1.5m_0$, where m_0 – electron mass [26,54]. We calculate the mean particle size for Samples 1 and 2, assuming that E_g is equal to 2.03 eV for selenium particles in a amorphous Se estimated above. The results are shown in Table 1.

In general, the photoluminescence peak of nanoparticles, organic dyes and inorganic quantum dots, is independent of the wavelength of

Table 1

Parameters of SeNPs, where $\langle E_g \rangle$ and $\langle E_b \rangle$ are mean band gap and exciton binding energy estimated from Figs. 5 and 6, $\langle d_{tauc} \rangle$ – mean nanoparticle diameter estimated using (4) from absorption spectra in Tauc plot, $\langle d_{abs} \rangle$ – mean nanoparticle diameter estimated using (6) (solid lines in Fig. 9), $\langle d_{em} \rangle$ – mean nanoparticle diameter estimated using (5) (columns in Fig. 9), $\langle d_{TEM} \rangle$ – mean diameter estimated by TEM in Fig. 2, QY – quantum yield of the samples calculated using (1).

Sample	$\langle E_g \rangle$, eV	$\langle E_b \rangle$, eV	$\langle d_{tauc} \rangle$, nm	$\langle d_{abs} \rangle$, nm	$\langle d_{em} \rangle$, nm	$\langle d_{TEM} \rangle$, nm	QY, %
Sample 1	2.80	0.08	4.5	4.4	4.3	4.0	4.7 ± 0.5
Sample 2	2.50	0.16	6.0	4.3	4.2	4.0	3.3 ± 0.6
Amorphous Se	2.03	0.25		6.3	6.1	8.5	

the excitation source because the excited electrons relax to the band edge before fluorescence begins regardless of their initial excitation energy. The luminescence peak wavelength is the same as long as the electrons are excited within the same band. In contrast, the luminescence peak of SeNPs exhibits a red-shift with an increase in the excitation wavelength. Currently a variety of models are proposed to explain the excitation-dependent emission. There are quantum confinement effect, surface traps, and giant red-edge effect [45].

The surface traps can cause an excitation dependent fluorescence due to the oxygen related groups, like –COH, –OH, and C–O–C with dangling bonds at the surface of nanoparticle, which may result in a series of traps having emission between π and π^* states of C=C in carbon containing nanoparticles [55]. The model of surface traps explains the excitation-dependent PL in oxide and carbon containing nanoparticles. However, functional groups, also sometimes described as molecular states, which are one of the most accepted surface trap states, in case of carbon and oxygen containing nanoparticles. However, in selenium containing nanoparticles these functional groups are regarded as non-radiative traps [56]. In addition, if the SeNPs luminescence is associated with surface traps, the band in the excitation spectrum associated with the polysaccharide should also shift, but it is not observed.

The giant red-edge effect was observed in non-polar solvents. Therein, the fluorescence of nanoparticles in a nonpolar solvent, such as pentane, exhibited relatively narrow and excitation-independent photoluminescence. Essentially, the red-edge effect is caused by the interaction between the solvent and nanoparticle dipoles [57].

In the quantum confinement effect the energy gaps of SeNPs are determined by the particle sizes – a smaller size leads to a wider energy gap. Therefore, the deviation of band gaps originating from the size distribution causes broadened emission wavelengths in the range 520–760 nm. The dependence of the mean exciton binding energy ($\langle E_b \rangle$) on the nanoparticle radius in an ensemble is shown in Fig. 8 based on data in Table 1. The mean exciton binding energy increases according to the law $\frac{1}{\langle d_{tauc} \rangle^{0.57}}$, where ($\langle d_{tauc} \rangle$) is the mean diameter of the ensemble of nanoparticles. This dependence of $\langle E_b \rangle$ ($\langle d_{tauc} \rangle$) is typical for nanoparticles in which quantum confinement is observed [58,59]. Thus, the shift of the excitation band to higher energies with a decrease in the size of SeNPs in Samples 1 and 2 can be caused by the quantum confinement effect. In our opinion, the quantum confinement effect successfully explains the shift of the PL at different excitation wavelengths in studied SeNPs. Assuming that maxima of excitation for such emission band (E_{ex}) correspond to the energy of first excited state of an exciton, the relationship between E_{ex} and its radius r using (3) and (4) is:

$$E_{ex} = E_g - E_b(r) + \frac{h^2}{8r^2} \left(\frac{1}{m_e^2} + \frac{1}{m_h^2} \right), \quad (5)$$

where $E_b(r)$ is the binding energy of SeNPs with radius r and E_{ex} – energy of the lowest exciton state determined from excitation spectra of SeNPs.

As pointed above, the luminescence in Se-NPs is attributed to the exciton emission. The annihilation of an exciton is accompanied by a characteristic luminescence due to radiative recombination of the

electron in conduction band with the hole valence band. Therefore, the intensity of luminescence band in Fig. 4 depends directly on number of particles with that size. Radius r of nanoparticle is calculated by Eq. (5), where E_{ex} is excitation peak energy for each emission band (5). $E_b(r)$ is determined using Fig. 8. All luminescence band intensities are normalized by intensity of luminescence most intense peaks at 620 nm in Sample 1 and 610 nm in Sample 2. The distributions are given in Fig. 9. The errors in radius calculation are determined by energy of excitation slits width. The spectral width in nanometers is permanently equal 10 nm, but in energy scale the slit widths depend on excitation wavelength.

For Sample 1 the mean diameter of SeNPs is about 4.3 nm, that is close to the mean diameter found by TEM in Fig. 2, b. Two peaks corresponding diameters 4.2 and 6.1 nm are found in the size distribution of Sample 2. In size distribution calculated from TEM data two peaks with 4.5 and 8 nm diameters are also observed (Fig. 2, d). The sizes of large nanoparticles of Sample 2 determined by two methods agree well within the specified error limit of luminescence method.

Alternatively, the size distribution $P(r)$ can also be obtained from analysis of the inhomogeneous broadening observed in the optical absorption spectra of nanocrystals. This method was proposed by Pesika et al. in Ref. [33]. Assuming that absorbance A at any energy is related to the total volume of particles with radius greater than or equal to the size corresponding to the absorption onset, $P(r)$ is given the follow relation [60]:

$$P(r) \cong -\frac{1}{V} \frac{dA}{dr} = -\frac{1}{4/3\pi r^3} \left[\frac{dA}{d\lambda} \cdot \frac{d\lambda}{dr} \right]_{\lambda=\frac{hc}{E_g(r)}} \quad (6)$$

Using Eq. (4) r is calculated for each point of absorption spectra. Fig. 9 shows a comparison of the distribution obtained from the absorbance using Eq. (6) (solid line) and luminescence spectra (columns). The results obtained from the TEM, absorption and luminescence spectra analysis show an excellent agreement. This demonstrates that the particle size distribution can be obtained from luminescence spectra.

4. Conclusion

We synthesized SeNPs in κ -CG shell. Luminescence properties of SeNPs were studied. It is found that luminescence of SeNPs is attributed to exciton emission. Polydispersity of SeNPs creates broadening of the absorption spectra and excitation dependent luminescence. We confirm this relationship by concluding the particle size distribution directly from the absorption and excitation-dependent luminescence spectra and comparing it to the distribution directly measured by TEM. We showed that analysis of excitation dependent spectrum allows to obtain a fairly accurate size distribution of nanoparticles if excitation-dependent luminescence is caused by quantum confinement effect. This analysis can be broadly applicable to a wide range of semiconductor systems.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jlumin.2019.03.056>.

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