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PHOTOLUMINESCENCE OF CdSe:Ni NANOPARTICLES OBTAINED BY CHEMICAL METHOD

Cadmium selenide nanocrystals doped with nickel were prepared in water phase chemistry technique with gelatin acting as capping agent. Structures were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), visible absorption and photoluminescence spectroscopies. Influence of component concentrations and technological parameters on nanocrystals average size and properties was studied.

I. Introduction

Colloidal CdSe nanocrystals can be used to create structures emitting in the entire visible light range, as a sensitizer for photopolymer cells and in biomedical visualization [1-7]. In comparison with organic fluorophores semiconductor nanocrystals are much more stable to photodegradation. Cadmium selenide nanocrystals exhibit strong quantum confinement and by regulating their size one can obtain emission in almost entire visible range. The wide practical application of this material is restrained by the high dispersion of the obtained particles and their instability. Therefore, the creation of a technology for the synthesis of stable nanoparticles with controlled size is relevant.

The hot-injection method proposed in [5] had instigated activity in the field of metal chalcogenide nanoparticles synthesis. It allowed to obtain highly luminescent crystals with good monodispersity but has certain disadvantages connected with expensive and hazardous pyrophoric reactives being used. Plenty of adaptations of original technology have been developed since then [6,7]. One of the natural choices of medium for QDs preparation might be polar solvents, for example water. Using this aqueous method, the energy level of CdSe QDs can be modified just allowing guest elements (Ag, Mn, Ni, Co etc.) into the CdSe host material and paves the way for discovering the new class luminescent materials with wide range of potential applications. Doping of these ions into the CdSe host material acts as the trap states for electrons and holes and enables the luminescence [8,9]. However, presence of two different kinds of ions simultaneously in a host material produces fluorescence which is totally different from the emission due to a single ion and this property is very useful for white and IR light generation [10].

In this paper, we report the synthesis of high-quality water-soluble CdSe:Ni nanocrystals colloidal method and discuss the influence of important experiment parameters (precursor concentration) on the optical and luminescent properties of prepared QDs. The synthesized CdSe and CdSe:Ni nanocrystals have been characterized absorption and luminescence spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), electron diffraction spectroscopy (EDS), and their morphology, crystal structure, optical properties, and element composition have been studied with these means. The prepared CdSe nanocrystals meet the requirements for the fluorescence materials in optoelectronics, biological labeling and will surely have promising applications in biochemical detection and biomedical researches.

II. Experimental

The study used commercially purshased reagents Merck Company. $CdCl_2$ was the source of cadmium ions. $NiCl_2$ was the source of cadmium ions in CdSe:NiThe source of Se^{2-} ions was sodium selenosulfate Na_2SeSO_3, Gelatin was used as the growth stabilizer of nanoparticles. The reaction at room temperature might be described as follows:

$$CdCl_2 + NiCl_2 + Na_2SeSO_3 \rightarrow$$
$$CdSe{:}Ni + SO_3 + 2NaCl + Cl_2\uparrow \quad (1)$$

The formation of CdSe is confirmed by the presence of diffraction maxima corresponding to the planes (002), (110), (001) in this material (Fig.1). The resulting colloidal solution containing CdSe, CdSe:Ni nanoparticles was deposited on quartz substrates, then the solvent evaporated, forming membranes for measuring optical absorption and photoluminescence. For investigation of structural properties the solvent sprayed on Si substrates.

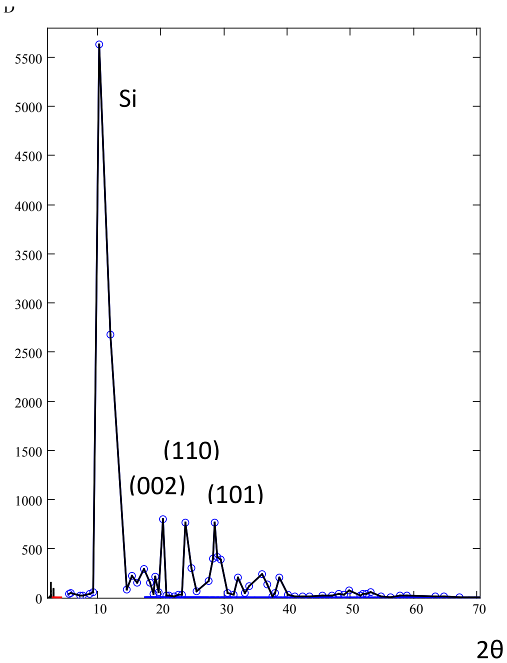

Fig. 1.X-ray diffraction pattern of CdSe nanoparticles

The SEM image was obtained via JEM-2100 (HR) transmission electron microscope (Japan Electron Optics Laboratory CO., Ltd.).

The optical absorption spectra in the visible range were recorded with MDR-6 (LOMO) monochromator with a 1200 grove·mm^{-1}. The photoluminescence spectra were recorded with ISP-51 (LOMO) quartz monochromator using LED (Edison Corporation) excitation on λ=400 nm.

The average size of the nanoparticles was estimated from the change in the band gap (ΔEg) relative to the bulk crystal, using the effective-mass approximation using the equation [5]

$$R = \frac{h}{\sqrt{8\mu\Delta E_g}} \quad (2)$$

There h is the Planck constant; $\mu=((m_{e*})^{-1}+(m_{h*})^{-1})^{-1}$, where $m_{e*}= 0.3me$, $m_{h*} = 0.6me$ are, respectively, the effective masses of the electron and hole in cadmium selenide, m_e is the mass of the free electron; ΔE_g is the difference between the width of the band gap in the nanoparticle and the bulk crystal of CdSe (1.7 eV).

III. Experiment and results

Investigations of CdSe:Ni nanocrystals optical absorption were carried out in the range of quanta of incident light 3.5-2 eV. The temperature of explored samples is varied from 77 to 300 K.

All investigated samples are characterized by the presence of a quantum-dimensional effect, which manifests itself in the high-energy shift of the fundamental absorption edge of the samples in comparison with the bulk CdSe absorption edge. Changing of the band gap width is confirmed by a change in solutions color from pale yellow to orange in comparison with the bulk crystals brown color. It is established that the shift magnitude is determined primarily by concentrations of cadmium and selenium precursors (Fig. 1). The highest shift is observed in samples containing 0.3% $CdCl_2$ and Na_2SeSO_3.

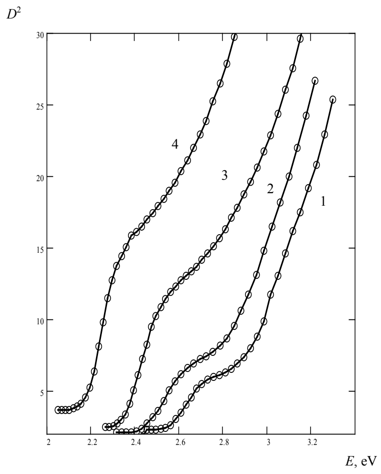

Fig.2. Optical absorption spectra of CdSe nanocrystals stabilized in gelatin matrices. Concentrations of CdC_{l2} and Na_2SeSo_3 is equal (1) 0.3%, (2) 0.5%, (3) 1%, (4) 2%. T_{meas}= 300 K.

By the magnitude of the fundamental absorption edge shift, the formula (2) calculated the size of CdSe nanoparticles. It is shown that when the precursor concentrations varied from 0.3 to 2%, the size of nanoparticles increases from 3 to 6 nm (see TABLE I).

As the nanocrystals temperature decreased from 300 to 77 K, the absorption edge shifted to the high-energy region by 0.14 eV. Such shift corresponds to a temperature change of CdSe band gap edge.

Table 1.
RESULTS OF CALCULATIONS OF cdse, cdse:ni NANOPARTICLES SIZES

No.	*$CdCl_2$, Na_2SeSo_3 concentrations*	*E_g, eV*	*ΔE_g, eV*	*R, nm*
1.	2%	2.25	0.55	5.6
2.	1%	2.60	0.9	4.4
3.	0.5%	2.81	1.11	3.8
4.	0.3%	2.93	1.23	3.5
5.	0.3%+$NiCl_2$ 0.001%	2.86	1.16	3.7
6.	0.3%+$NiCl_2$ 0.005%	2.77	1.07	3.9
7.	0.3%+$NiCl_2$ 0.01%	2.7	1	4.2

The doping of nanocrystals with nickel leads to a shift of the absorption edge to a region of lower energies, which is explained both by an increase in the size of nanoparticles and by inter-impurity Coulomb interaction.

The photoluminescence spectra of the investigated CdSe nanocrystals are characterized by emission band localized in the visible spectral region. The half-width of the photoluminescence spectrum varied from 50 to 70 nm, depending on $CdCl_2$ and Na_2SeSO_3 concentration (Fig.3).

It is established that the position of these emission lines is determined by the concentration of $CdCl_2$ and Na_2SeSO_3 in solution. The position of the emission maxima varied from 2.54 to 2.14 eV with an increase in concentrations of $CdCl_2$ and Na_2SeSO_3 from 0.3 to 2%.

The position of the observed emission lines correlates with the second linear region position of the corresponding optical absorption spectrum. The magnitude of the Stokes shift in the samples under study is 20-30 meV.

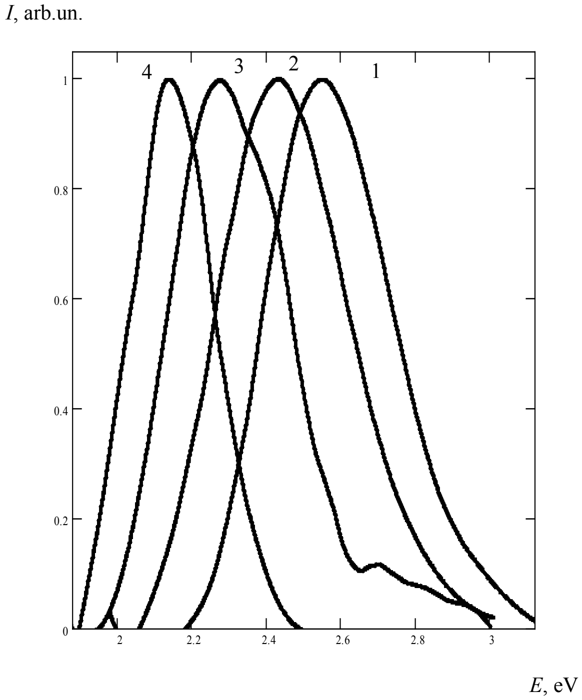

Fig. 3. Photoluminescence spectra of CdSe nanocrystals stabilized in gelatin matrices. Concentrations of CdCl2 and Na2SeSo3 is equal (1) 0.3%, (2) 0.5%, (3) 1%, (4) 2%. Tmeas=300 К.

When the temperature of nanocrystals changes from 300 to 77 K, the emission lines shift to the high-energy region by 0.14 eV, which corresponds to a temperature change of CdSe band gap. This allows us to assume that transitions involving excitons are responsible for these lines. Lines of a similar nature were observed earlier in [2].

With an increase of precursors concentration, broadening of the emission lines and the appearance of additional high-energy radiation maxima are observed. This is explained by the spread in the sizes of the nanoparticles obtained. SEM images of the investigated nanocrystals (Fig.4) showed that the size of nanoparticles can vary within the limits of 2-6 nm.

The exciton emission spectra of the CdSe:Ni are shifted to the region of lower energies (Fig.5). There is a complete correlation with the absorption spectra shown in as the nickel concentration increases. At the same time, nickel doping results in a series of emission lines in the visible and near-IR regions.

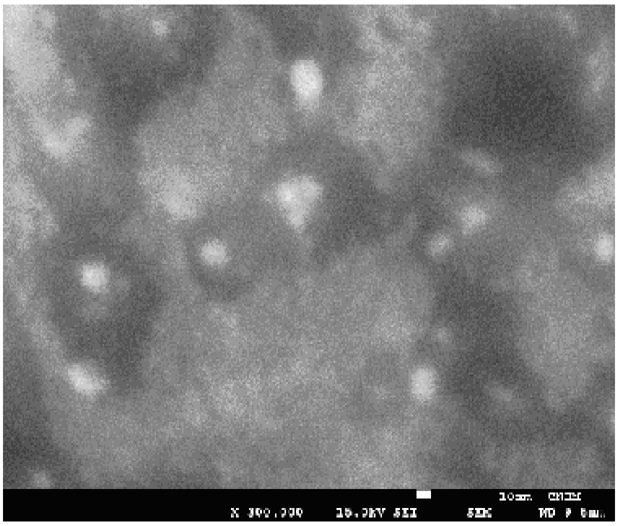

Fig. 4. SEM image of CdSe nanocrystals with 0.5% precursor concentration.

The luminescence spectra of nanocrystals in the visible region are characterized by lines localized at 2.47, 2.38, 2.28, and 2.15 eV. In the near-IR region, the photoluminescence spectra of Sdce nanocrystals show three emission lines at 1.86, 1.74, and 1.64 eV. The position of these lines remained unchanged with an increase in the concentration of $NiCl_2$, and their intensity increased. This behavior is characteristic of emission lines due to intracenter radiative transitions.

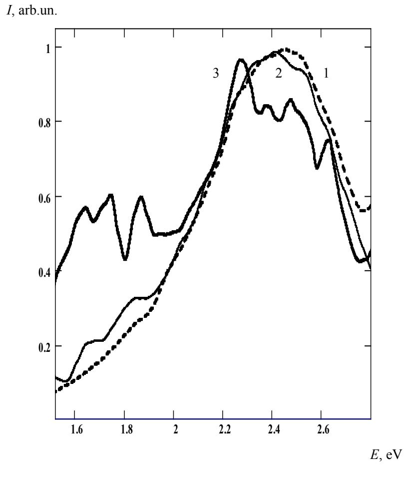

Fig. 5. Photoluminescence spectra of CdSe:Ni nanocrystals. Concentrations of NiC_{12} is equal (1) 0.001%, (2) 0.005%, (3) 0.01%, Tmeas=300 K. CdC_{12}, Na_2SeSo_3 concentrations is equal 0.3%.

The luminescence of bulk crystals of ZnSe:Ni was previously investigated [11]. The band gap is varied in the range of 2.8–2.5 eV, depending on the nickel impurity concentration in these crystals. We assume that the visible emission lines are due to the emission transitions from the excited states $^1E(G)$, $^1T_1(G)$, $^1A_1(G)$, $^1T_2(G)$ to the ground state $^3T_1(F)$ of the Ni^{2+} ion.

The near-IR emission lines are due to transitions from the excited state $^3T_1(P)$ split by the spin-orbital interaction to the ground state $^3T_1(F)$ of the Ni^{2+} ion.

Thus, the luminescent properties of the CdSe:Ni nanocrystals are controlled by the intracentre emission transitions within the Ni^{2+} ion.

The obtained results indicate the possibility of controlling the nanoparticles size by different methods. The obtained samples have effective emission in the visible and near-infrared region can be used as the sensitizer for photopolymer cells.

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Abstract–Cadmium selenide nanocrystals doped with nickel were prepared in water phase chemistry technique with gelatin acting as capping agent. Structures were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), visible absorption and photoluminescence spectroscopies. Influence of component concentrations and technological parameters on nanocrystals average size and properties was studied.

Key words – Cadmium Selenide, Nanocrystals, Absorption Edge, Photoluminescence.

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ФОТОЛЮМІНЕСЦЕНЦІЯ НАНОЧАСТИНОК CdSe:Ni ОТРИМАНИХ ХІМІЧНИМ МЕТОДОМ

Анотація–Нанокристали CdSe, леговані нікелем, були отримані в водній фазі з додаванням желатину як зв'язуючого агенту. Структурні властивості були досліджені за допомогою дифракції рентгенівських променів (XRD), скануючої електронної мікроскопії (SEM), видимого поглинання та фотолюмінесцентної спектроскопії. Визначено вплив концентрації компонентів та технологічних параметрів на середній розмір нанокристалів та досліджено їх властивості.

Ключові слова – Селенід кадмію, нанокристали, край поглинання, фотолюмінесценція.

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ФОТОЛЮМИНЕСЦЕНЦИЯ НАНОЧАСТИЦ CdSe:Ni ПОЛУЧЕННЫХ ХИМИЧЕСКИМ МЕТОДОМ

Аннотация – Нанокристаллы CdSe, легированные никелем, были получены в водной фазе с добавлением желатина в качестве связывающего агента. Структурные свойства были исследованы при помощи дифракции рентгеновских лучей (XRD), сканирующей электронной микроскопии (SEM), видимого поглощения та фотолюминесцентной спектролскопии. Определено влияние компонентов и технологических параметров на средний размер нанокристаллов и их свойства.

Ключевые слова – селенид кадмия, нанокристаллы, край поглощения, фотолюминесценция.