

Comparison of Characteristics of Thermostimulated Luminescence of CdS Nanostructures Obtained by Green Synthesis and Chemical Method

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CdS nanoparticles obtained by green synthesis in biosystems of the basidiomycete fungus *Pleurotus ostreatus* and roots of *Linaria maroccana* were studied for the first time by the method of thermoluminescence (TL) in the temperature range 80-400 K. To compare the TL characteristics of CdS nanoparticles obtained by green synthesis with others, samples of two types of CdS, of nano- and micro-sizes, grown by chemical methods, were studied. Since the luminescence intensity was low and the integral TL curve was practically not divided into elementary peaks, activation energies were determined by the form of elementary TL curves, which were obtained by decomposing the integral curve into elementary contours according to the formulas for linear and quadratic TL kinetics. It was found that the values of activation energy of traps of CdS nanoparticles obtained by green synthesis are in the range of 0.09-0.53 eV, which correlates with the obtained values of activation energy for the corresponding TL bands of CdS samples obtained by chemical methods (0.07-0.62 eV). For all types of CdS samples, the TL curves have a similar shape and almost one composition of elementary peaks, which differ only in the intensity distribution of individual peaks. That is, regardless of the method of particle synthesis, they have a similar defective structure, and, accordingly, a similar nature of TL. In general, based on TL studies, it is concluded that CdS nanoparticles obtained by green synthesis are of sufficient quality, in their defective structure they are almost indistinguishable from CdS nanoparticles obtained by traditional chemical methods, and is a promising material for widespread use, and such CdS is a relatively environmentally friendly material.

Keywords: Thermostimulated luminescence, CdS nanoparticles, Green synthesis, Traps, Activation energy.

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1. INTRODUCTION

Nanocrystals based on semiconductor materials, due to such properties as high quantum radiation yield and high mechanical strength, are now widely used in various fields of opto- and nanoelectronics, in particular, as fluorescent labels for medical diagnostics.

The synthesis of nanoparticles requires three main components: soluble medium, reducing and stabilizing substances. Traditional methods for obtaining CdS nanoparticles are environmentally hazardous, highly expensive and complex. Green synthesis is a method for obtaining metal nanoparticles of various morphologies from salts of the corresponding metals using plant extracts as reducing and stabilizing agents. Due to the variety of plant extracts, types of metal salts and the ability to change the composition of the mixture, in which the reaction takes place, as well as the reaction conditions, it is possible to create nanoparticles of different shapes and sizes (from 10 to 500 nm) [1, 2].

Among other media for the biotechnological synthesis of CdS nanoparticles, the use of biosystems of the basidiomycete fungus *Pleurotus ostreatus* and the root system of the plant *Linaria maroccana* is important [3]. The efficiency of using fungal systems for the synthesis of CdS nanocrystals is justified by the presence of sulfate reductase enzymes in fungi, which carry out the reduction of sulfate groups of metal salts directly in the culture medium. The result is the extracellular formation of CdS nanoparticles, which by their characteristics are quantum dots. In addition, fungi have a high

productivity of synthesis and secretion of enzymes, protein and hydrocarbon compounds, are characterized by antibacterial and antitumor activity, their extracts are an important raw material for the manufacture of drugs. The introduction of technologies for the industrial synthesis of quantum dots using fungi involves obtaining a high yield of nanoparticles. Regarding plant systems, for biological synthesis of semiconductor nanoparticles, including *Linaria maroccana*, it should be noted that they have certain advantages over microorganisms due to the presence of secondary metabolites that form a protective organic coating that prevents the aggregation of quantum dots [4]. The use of plant extracts is the safest, most environmentally friendly and affordable approach to obtain nanoparticles.

As with CdS particles of chemical origin, green CdS particles require the study of their defective structure. The thermoluminescence (TL) method is one of the main methods for studying defects in crystals. The advantage of the method is its significant sensitivity, accuracy (almost unattainable for other research methods), clarity of results and relative simplicity of experiments. The TL curves of green CdS nanoparticles were obtained and analyzed in the work, and the thermal activation energies of traps were determined. The characteristics of the obtained TL curves for CdS nanoparticles obtained by green synthesis with the corresponding values for CdS nanoparticles synthesized by chemical methods were compared.

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2. EXPERIMENTAL TECHNIQUE

Thermoluminescence. The TL study of nanocrystalline CdS was performed in the temperature range of 80-450 K. The samples were placed in a vacuum cryostat and excited at a temperature of 77 K by X-rays (BSV-2, W, 30 kV, 10 mA) through a beryllium window 0.5 mm thick. The duration of excitation varied and was 20-60 min. The heating rate of the sample was $0.2 \pm 5\%$ K/s. The integral intensity of TL in the PEM sensitivity region (300-800 nm) was measured. Experimental data were recorded and processed using specially designed programs.

Samples. CdS nanoparticles obtained by green synthesis in the biosystems of the basidiomycete fungus *Pleurotus ostreatus* and the root system of the plant *Linaria maroccana* were used (synthesis is described in detail in [3, 5, 6]). It was determined by transmission electron microscopy (TEM) that CdS nanoparticles (actually, quantum dots) form dense clusters with a size of 40-70 nm. The size of individual nanoparticles within these clusters is 5-8 nm.

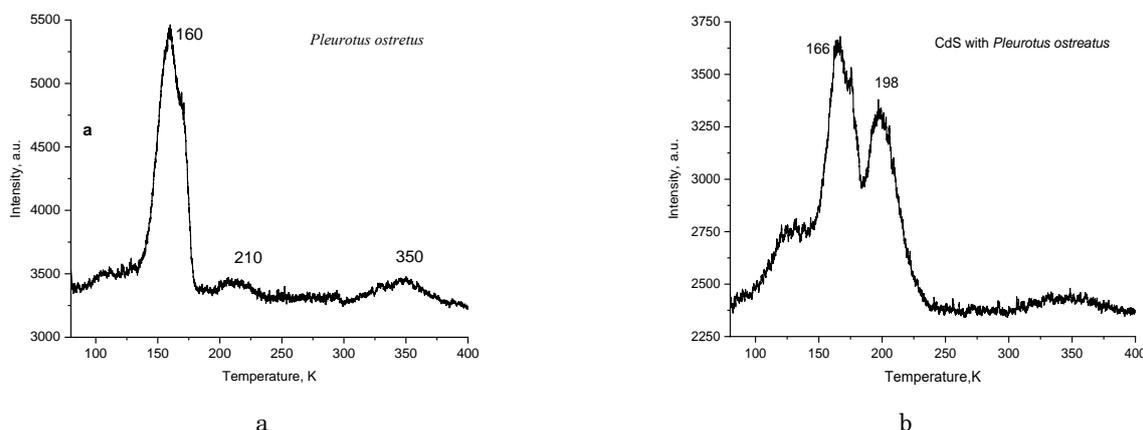


Fig. 1 – TL curve for the fungal system *Pleurotus ostreatus* (a), TL curve for CdS nanoparticles obtained by green synthesis without separation of the fungal system (b)

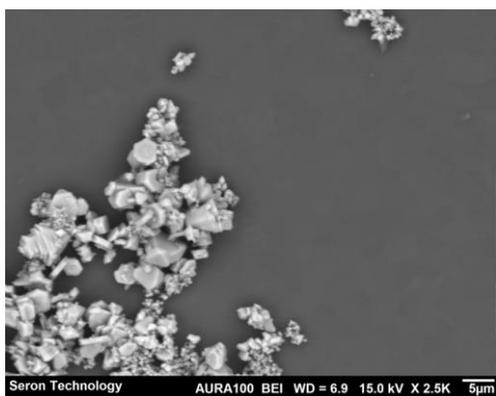


Fig. 2 – SEM-image of CdS type II micropowder

To compare the TL characteristics of CdS nanoparticles obtained by green synthesis with others, samples of two types were taken. Type I – CdS nanoparticles grown chemically in a two-phase water-toluene system; the average particle size – 2.0 ± 0.5 nm – was determined by the absorption spectra from the dependence of the exciton transition energy on the size of the nano-

particle [7]. Type II – micropowder; scanning electron microscopy (SEM) determined that the micropowder has a fairly large scatter in size – from hundreds of nanometers to 6-8 microns; average size - units of microns (Fig. 2). For TL studies, type I and II samples were prepared according to the described procedure, but without preheating the substrate.

To prepare samples for TL studies from CdS nanoparticles obtained by green synthesis, a copper plate was used, on which a filtered solution of CdS nanoparticles was applied so that they tightly filled the surface with a size of $\sim 10 \times 10$ mm. The samples were dried, and the procedure was repeated until the desired sample thickness was obtained. When recording the TL curves, the glow of the bio-environment (i.e., the basic fungal and root systems) was registered, which exceeded the glow of pure CdS. Therefore, before the sample was made, the copper plate was heated to about 400 K, this temperature was maintained, and a solution of CdS nanoparticles was applied to the plate. Thermal destruction of the biosystem took place, and after such a procedure the glow of the bioenvironment was neglected in comparison with the glow (also weak) of CdS (see Fig. 1). The result is CdS samples suitable for TL studies and, in particular, comparison with the parameters of CdS TL curves synthesized by other methods. However, such CdS samples have not yet been studied by photoluminescence and electron absorption.

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3. RESULTS AND DISCUSSION

Figures 3-5 show the typical dependences of the integral TL intensity on the temperature of the sample for nanocrystalline CdS obtained by green synthesis and chemical methods (as well as the decomposition of the TL curves into elementary peaks, see below). The samples were irradiated with X-rays for 20-60 min at nitrogen temperature (77 K).

The TL curves for all CdS samples can be divided into three regions: low-temperature, medium-temperature and high-temperature. For the low-temperature region (80-200 K) the most intense band is at ~ 110 K. In the middle region (200-270 K) there is a complex undivided band with a maximum of ~ 220 K.

The high-temperature region (270-400 K) has a maximum at ~ 330 K. The position of the visible maxima of the bands are given in Table 1.

For nanoparticles obtained by green synthesis by the fungal system *Pleurotus ostreatus*, the intensity of the TL bands depends on the excitation time. With short-term excitation (up to 10 min), the most intense is the band in the region of medium temperatures. As the excitation duration increases (up to 30 min), the system of low-temperature bands (up to 200 K) becomes dominant, and the high-temperature region is equalized in intensity with the region of medium temperatures (Fig. 3). With increasing excitation time, the intensity of TL as a whole increases, but differently for

the selected three areas. After 30 min of excitation, the intensity of TL almost reaches saturation. This can be explained by the different rates of formation of defects and accumulation of light sum on the traps. For nanoparticles synthesized using the root system of *L. Maroccana*, the intensity of low-temperature and high-temperature bands is approximately the same (Fig. 4), the appearance of the curves is weakly dependent on the irradiation time. For nanoparticles obtained by chemical methods, in both cases the intensity is dominated by a low-temperature band (Fig. 5). The positions of the band maxima for all types of CdS samples are generally correlated.

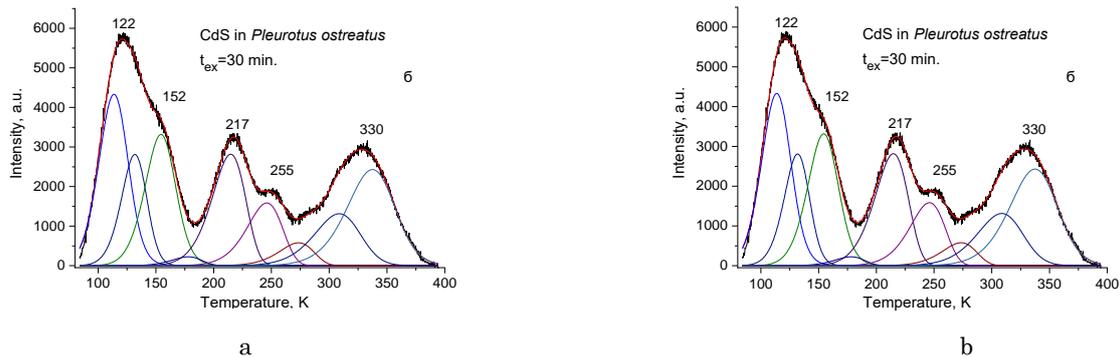


Fig. 3 – Typical TL curves of nanocrystalline CdS grown by green synthesis using the fungal system *Pleurotus ostreatus* (irradiation time: a) 10 min, b) 30 min)

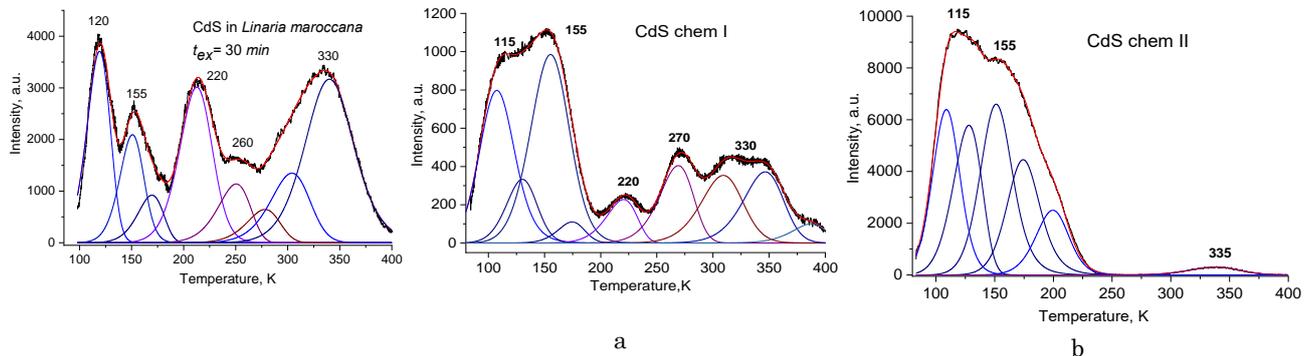


Fig. 4 – Typical TL curve of nanocrystalline CdS grown by green synthesis (type II, b) obtained by chemical methods using the roots of *Linaria maroccana* (irradiation time 30 min)

Table 1 – Position of maxima of complex TL bands for investigated samples

CdS type	Position of maxima of complex bands, K				
Nanoparticles, green synthesis, <i>Pleurotus ostreatus</i>	~ 122	152	~ 217	255	330
Nanoparticles, green synthesis, <i>Linaria maroccana</i>	120	155	220	~ 260	~ 330
Nanoparticles, chemical method (type I)	~ 115	155	220	~ 270	~ 330
Micropowders, chemical method (type II)	115	155	–	–	335

Some differences in the position of the maxima of the corresponding peaks (up to 10 K) and their intensities for different samples can be explained by different sampling technology (rather than size), as well as slightly different electronic structure of defects that cause TL.

Methods for determining the activation energy were described in detail in [8-10]. In this case, since the intensity of TL was insignificant, and the integral

curve of TL was practically not divided into elementary peaks, the most effective method was to determine the activation energy by the shape of the elementary curve of TL. For the determination of activation energies of individual TL peaks by this method, as well as for comparative analysis, TL curves with complex contours were decomposed into elementary components using program *PeakFit* according to formulas (1) and (2) for linear and quadratic kinetics, respectively [8]. For each

peak, the activation energy, frequency factor and temperature of a maximum were determined as approximation parameters of experimental curves by analytic

$$I(T) = -\frac{dn}{dt} = n_0 p_0 \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{p_0}{\beta} \left(\int_{T_0}^T \exp\left(-\frac{E}{kT}\right) dT\right)\right], \quad (1)$$

$$I(T) = -\frac{dn}{dt} = n_0 p_0 \exp\left(-\frac{E}{kT}\right) \left[1 + \frac{p_0}{\beta} \left(\int_{T_0}^T \exp\left(-\frac{E}{kT}\right) dT\right)\right]^{-2}. \quad (2)$$

Here n_0 is the initial concentration of carriers on the traps (light sum), p_0 is the frequency factor, β is the heating rate, E is the energy of thermal activation of the trap; n_0 , p_0 , E are the parameters of the decomposition corresponding to the minimum standard deviation (SCR) of the analytical curve from the experimental one. Using the decomposition into elementary contours, the values of activation energy of traps of TL curves of CdS nanoparticles obtained by green synthesis using the fungal system *Pleurotus ostreatus* and the roots of *Linaria maroccana* were determined. It was found that they lie in the range of 0.09-0.53 eV. The activation energies of traps of the corresponding bands of the TL

ones. The shape of each contour for agreement with the experimental curves was chosen according to the equations of linear or quadratic TL kinetics:

curve for CdS nanoparticles obtained by the chemical method of type I are in the range of 0.07-0.62 eV. For CdS micropowders obtained by the type II chemical method, the values of the activation energy of the traps were calculated for the low-temperature band and the medium-temperature band as for one wide inseparable band of the TL curve. The values are in the range of 0.09-0.52 eV, which correlates with the obtained values of the activation energy of traps for other types of CdS samples. Due to the low intensity of the TL band in the high-temperature region, it is impossible to obtain the activation energy value for CdS micropowders (type II). The obtained values are shown in Table 2.

Table 2 – Activation energies of traps in CdS

Samples, excitation time, peak position, activation energies										
CdS (P.ostreatus) 30 min	T , K	114	132	154	178	215	246	273	309	337
	E_{act} , eV	0.09	0.14	0.17	0.20	0.26	0.33	0.42	0.43	0.52
CdS (P.ostreatus) 25 min	T , K	112	131	152	178	214	244	271	316	339
	E_{act} , eV	0.09	0.14	0.18	0.20	0.27	0.33	0.42	0.44	0.52
CdS (P.ostreatus) 20 min	T , K	110	130	154	181	216	247	279	313	340
	E_{act} , eV	0.09	0.14	0.18	0.20	0.29	0.33	0.42	0.44	0.52
CdS (P.ostreatus) 10 min	T , K	112	131	152	178	214	244	271	316	339
	E_{act} , eV	0.09	0.14	0.18	0.20	0.27	0.33	0.42	0.44	0.52
CdS (L.maroccana) 40 min	T , K	116	124	151	176	214	248	–	304	341
	E_{act} , eV	0.11	0.14	0.17	0.20	0.27	0.34	–	0.44	0.53
CdS (L.maroccana) 30 min	T , K	119	131	151	169	213	251	278	304	340
	E_{act} , eV	0.10	0.14	0.18	0.19	0.27	0.33	0.43	0.44	0.52
CdS chem. (type I)	T , K	108	130	155	175	221	–	269	309	347
	E_{act} , eV	0.07	0.11	0.12	0.23	0.29	–	0.42	0.49	0.62
CdS chem. (type II)	T , K	109	128	151	174	200	–	–	–	338
	E_{act} , eV	0.09	0.11	0.17	0.23	0.28	–	–	–	0.52

Regarding the nature of TL. In structures of type $A_{II}B_{VI}$, in particular CdS, typical defects are Frenkel pairs – interstitial atoms Cd^+ or S^- and the corresponding vacancies V_{Cd}^- , V_S^+ . Such pairs correspond to the donor and acceptor energy levels in the forbidden zone. The nonzero charge state of these defects is caused mostly by a high probability of formation of a charged pair of defects in the reaction $CdS \rightarrow V_S^+ + V_{Cd}^-$.

There are radiative transitions of an electron from the donor Cd_i^+ or the conduction band to the center S_i^- from the group of levels (V_S^+, Cd_i^+) to the valence band. As the excitation increases, the processes of defect generation and ionization of donors and acceptors occur more intensively. The hole (S_i^-) and the electron (Cd_i^+) are transferred to the valence band and the conduction band, respectively, which leads to a redistribution of

intensities of luminescence bands. There is also a wide band, which can be formed by radiative transitions between charged vacancies of sulfur and cadmium, i.e., in a close donor-acceptor pair (V_S^+, V_{Cd}^-) . After radiation, these defects can be annihilated according to the scheme $(V_{Cd}^{2-} + Cd_i^{2+})$ or $(V_S^{2+} + S_i^{2-})$.

For all types of CdS samples, the TL curves have a similar shape and almost one set of elementary peaks, which differ only in the distribution of intensities of individual peaks of TL. Thus, regardless of the method of synthesis of nanoparticles, they all have a similar defective structure, i.e., the crystal structure and electronic structure of defects, and, accordingly, a similar nature of TL. Since the activation energy of the trap is determined mainly by the interaction with the immediate environment, these defects are typical, the most common defects in such structures, namely the vacan-

cies of sulfur and cadmium or their atoms in the inter-nodal position. As follows from the analysis of these and previously obtained results for CdS, CdSe, CdSSe structures [11], low-temperature peaks are most likely due to cadmium vacancies, and high-temperature peaks are due to sulfur vacancies. This is also confirmed by the results of [12], where thermally stimulated luminescence of bulk CdS annealed in cadmium, sulfur, and air was studied.

4. CONCLUSIONS

For the first time, CdS nanoparticles obtained by green synthesis (temperature range 80-400 K) were studied by the TL methods. The TL curves for all studied CdS samples can be conditionally divided into three regions: low-temperature region (80-200 K), medium-temperature region (200-270 K), and high-temperature region (270-400 K). For "green" nanoparticles, the relative intensity of the TL bands in these temperature ranges depends on the excitation time and equalizes with increasing irradiation time, which is explained by the different rates of defect formation and light sum accumulation on the traps.

The energy of thermal activation of traps in CdS was determined: for nanoparticles obtained by green synthesis using the fungal system *Pleurotus ostreatus* and the root system *Linaria maroccana*, the range of values is 0.09-0.53 eV; for "chemical" nanoparticles of type I – 0.07-0.62 eV, and "chemical" micropowders of type II – 0.09-0.52 eV. Frequency factors are in the range of 10^4 - 10^6 s⁻¹, except for the lowest temperature peak (110-120 K), for which it is about 10^3 s⁻¹.

Regarding the nature of TL, for CdS nanoparticles obtained by green synthesis, the defective structure is similar to that in "chemical" nanoparticles: the low-temperature TL bands are caused by simple defects formed by cadmium vacancies, the high-temperature TL bands are caused mostly by sulfur vacancies.

In general, on the basis of TL studies, it can be concluded that CdS nanoparticles obtained by green synthesis using the fungal system *Pleurotus ostreatus* and the roots of *Linaria maroccana* are of sufficient quality, in their defective structure they are almost indistinguishable from CdS nanoparticles obtained by traditional chemical methods, and is a promising material for widespread use, and such CdS is a relatively cheap and relatively environmentally friendly material.

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Порівняння характеристик термостимульованої люмінесценції наноструктур CdS, отриманих зеленим синтезом та хімічним методом

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Методом термолюмінесценції (ТЛ) в інтервалі температур 80-400 К вперше досліджено наночастинки CdS, отримані зеленим синтезом в біосистемах базидіального гриба *Pleurotus ostreatus* та коренів льонку *Linaria maroccana*. Для порівняння характеристик ТЛ наночастинок CdS, отриманих зеленим синтезом з іншими, досліджено зразки двох типів CdS, нано- та мікророзмірів, вирощених хімічними методами. Оскільки інтенсивність люмінесценції була незначною, а інтегральна крива ТЛ практично не розділялась на елементарні піки, енергії активації визначались за формою елементарних кривих ТЛ, які отримувались в результаті розкладу інтегральної кривої на елементарні контури згідно формул для лінійної та квадратичної кінетики ТЛ. Встановлено, що значення енергії активації пасток кривих ТЛ наночастинок CdS, отриманих зеленим синтезом, лежать в межах 0.09-0.53 eV, що корелює з отриманими значеннями енергії активації для відповідних смуг ТЛ зразків CdS, отрима-

них хімічними методами (0.07-0.62 eV). Для всіх типів зразків CdS криві ТЛ мають подібну форму і практично один склад елементарних піків, які відрізняються лише розподілом інтенсивностей окремих піків. Тобто, незалежно від методу синтезу частинок, вони мають подібну дефектну структуру, і, відповідно, подібну природу ТЛ. В цілому, на підставі ТЛ досліджень робиться висновок, що наночастинки CdS, отримані зеленим синтезом за допомогою *Pleurotus ostreatus* та *Linaria maroccana* є достатньо якісними, за своєю дефектною структурою вони практично не відрізняються від наночастинок CdS, отриманими традиційними хімічними методами, і є перспективним матеріалом для широкого застосування, причому такий CdS є порівняно екологічним матеріалом.

Ключові слова: Термостимульована люмінесценція, Наночастинки CdS, Зелений синтез, Пастки, Енергія активації.